Fluorinated-l,2,3-triazines and related systems

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UNIVERSITY OF DURHAM

A THESIS

Entitled

FLUORINATED-1,2,3-TRIAZINES AND RELATED SYSTEMS

Submitted by

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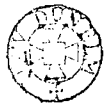
A Candidate for the Degree of Doctor of Philosophy
1984



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Finally, but not least, my thanks go to my parents for their devotion and encouragement.

MEMORANDUM

The work described in this thesis was carried out in the University of Durham, and is original except where specifically stated by reference.

It has not previously been submitted either wholly, or in part, for a degree at this or any other university.

Part of this work has been the subject of a paper presented at the 186th American Chemical Society National Meeting at Washington D.C., U.S.A., August 1983.

SUMMARY

Synthesis of fluorinated-1,2,3-triazines have been developed from trichloro-1,2,3-triazine. Stepwise vapour phase fluorination over KF gave trifluoro- and 5-chloro-4,6-difluoro-derivatives. Polyfluoroalkylation of both trichloro- and trifluoro-1,2,3-triazines with hexafluoropropene led to formation of perfluoro-4,6-bisisopropyl- and-4,5,6-trisisopropyl-derivates, together with an unusual product.

Generation of azetes has been investigated in the photolytic as well as thermal elimination of nitrogen from the fluorinated triazines. Trifluoro-derivative gave trifluoroacrylonitrile on thermolysis and poly(trifluoroazete) on photolysis. The trifluoroazete was observed at 77K and trapped as a copolymer with hexafluorobut-2-yne. Perfluorotrisisopropyl-derivative yielded fragmentation products, *i.e.* perfluoro-isobutyronitrile and -2,5-dimethylhex-3-yne on photolysis as well as on thermolysis.

Static thermolysis of perfluoro-4,6-bisisopropyl-1,2,3-triazine resulted in formation of perfluoro-2,4,5-trisisopropylpyrimidine and -2,4,6-trisisopropylpyridine, and a dimer of perfluoro-2,4-bisisopropylazete, whereas on flash pyrolysis perfluoro-3-methylbut-1-yne and -isobutyronitrile were obtained. Perfluoro-3-methylbut-1-yne reacted with 2,3-dimethylbuta-1,3-diene to yield 1:1 adducts.

Photolysis of perfluoro-4,6-bisisopropyl-derivative led to quantitative formation of the dimer of perfluoro-2,4-bisisopropylazete, *i.e.*, perfluoro-2,4,6,8-tetrakisisopropyl-1,5-diazatricyclo[4,2,0,$O^{2,5}$]octa-3,7-diene, which was pyrolyzed to yield perfluoro-isobutyronitrile and -2,4,6-trisiso-

propylpyridine. Perfluoro-2,4-bisisopropylazete has been trapped as 1:1 adducts with furan, and as perfluoro-2,4-bisisopropylpyridine which was derived from a cross-dimer with trifluoroazete. Both results provide the first clear evidence that a monocyclic azete has been trapped chemically. A mixture of dimers of perfluoro-2,4-bisisopropylazete was obtained on low temperature photolysis.

Formation of the unusual product, *i.e.*, perfluoro-2,4,6-trisisopropyl-5-isopropylidene-1,2,3-triazacyclohexa-3,6-diene during polyfluoroalkylation, has been shown to involve nucleophilic attack of perfluoroisopropylanion on the nitrogen at the 2-position of perfluoroisopropyl-1,2,3-triazine. Nucleophilic attack of bases on the nitrogen also occurred to give novel derivates, which include stable intramolecular zwitterions and a thermal [4+4] cycloadduct, *i.e.*, 2,2-dialkyl-4,5,6-tris-heptafluoroisopropyl-1,3-diaza-2-azaniacyclohexadienides and 6,7,10-trisheptafluoroisopropyl-3,4-dimethyl-1,8,9-triaza-[4,2,2]octa-3,7,9-triene, respectively.

Various derivatives of the unusual product were obtained by cycloaddition, radical addition and nucleophilic reactions. Also obtained were fluorinated allenes on pyrolysis.

CONTENTS

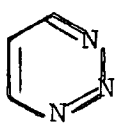
INTRODUCTION

CHAPTER ONE

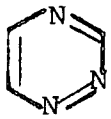
SYNTHESIS AND CHEMISTRY OF 1,2,3-TRIAZINES

1.1 Introduction

There are three families of triazines, which are the 1,2,3-(1), 1,2,4-(2), and 1,3,5-(3) triazines. Preparation of the parent compounds have been known for (3) and sometimes



(1)



(2)

(3)

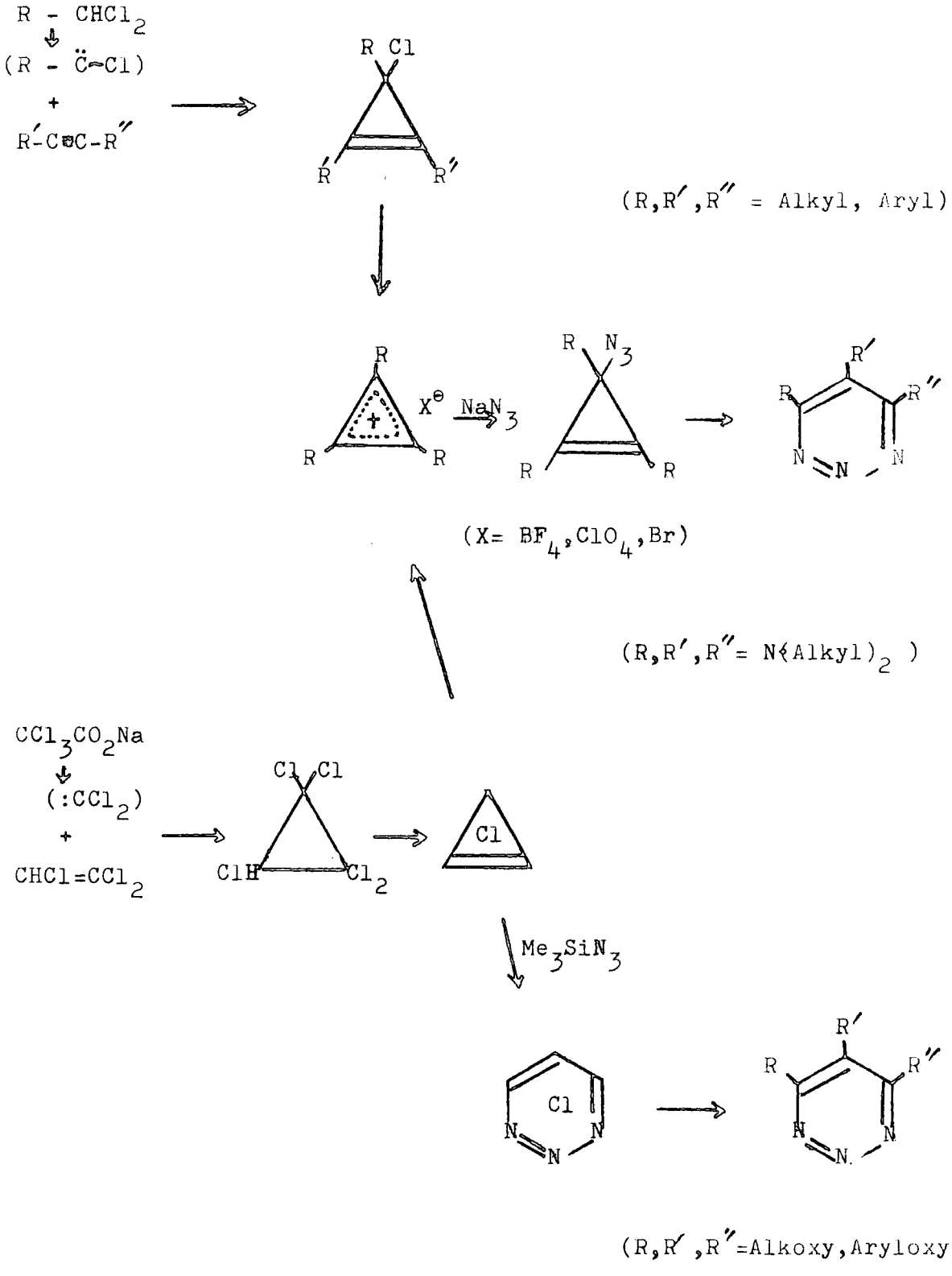
for (2) but the compound (1) has only recently been prepared. There are only a small number of papers dealing with the synthesis or reactions of unfused 1,2,3-triazine systems, though fused derivatives have been widely investigated.[1,2]

1.2 Synthesis of 1,2,3-Triazine

The reported routes to unfused 1,2,3-triazines are (A) thermal rearrangement of cyclopropenyl azides,[2] (B) oxidative ring expansion of N-aminopyrazoles,[3] and (C) reaction of diazomethane with chloroazirines.[4]

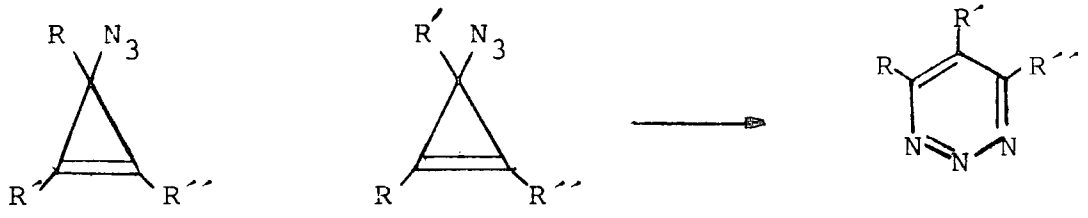
(A) Thermal rearrangement of cyclopropenyl azides

This method has been most widely used for the preparation of trisubstituted-1,2,3-triazines.[2] The reactions may be summarized by the following examples.



(R,R',R''=Alkoxy,Aryloxy)

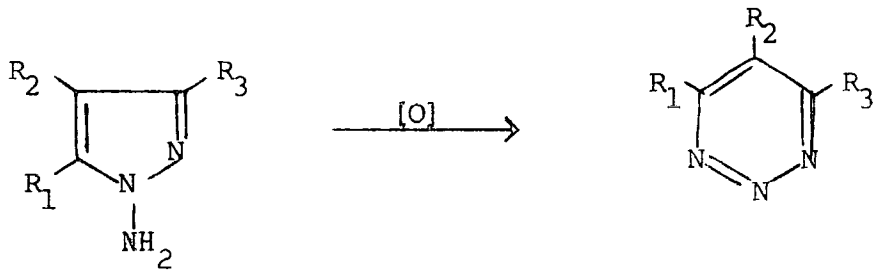
Cyclopropenylazide with two different substituents yields a single 1,2,3-triazine with strongest electron donating substituents in the 5-position.[5] Synthesis of 4,5,6-tris(tert-butyl)- 1,2,3-triazine *via* the corresponding azide was attempted without success.[6]



(R = R'' = C_6H_5, R' = 4-Me-C_6H_4 or 4-MeO-C_6H_4)

(B) Oxidative ring expansion of N-aminopyrazoles

The procedure, originally developed by Rees *et al*[7] for the preparation of 1,2,3-benzotriazine, has been successfully used for the first synthesis of the parent compound but using a different oxidizing agent.[3] Mono- and di-substituted-1,2,3-triazines were also synthesized by this procedure.



(a) $R^1 = R^2 = R^3 = H$

(b) $R^1 = R^2 = H$, $R^3 = Me$

(c) $R^1 = Me$, $R^2 = R^3 = H$

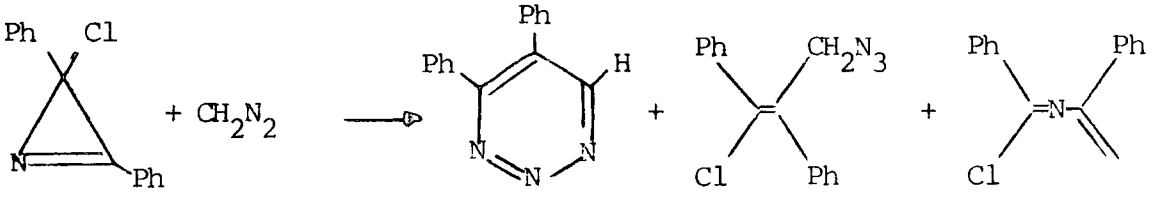
(d) $R^1 = R^3 = Me$, $R^2 = H$

(e) $R^1 = Ph$, $R^2 = H$, $R^3 = Me$

(f) $R^1 = R^2 = R^3 = Me$

(C) Reaction of diazomethane with chloroazirine

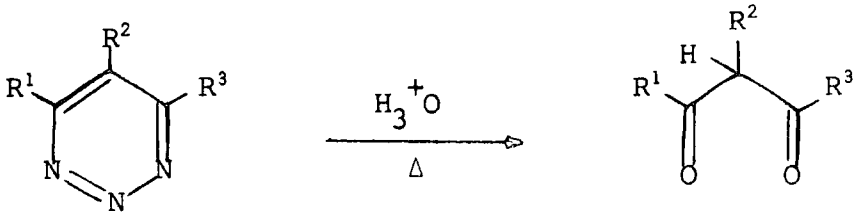
4,5-Diphenyl-1,2,3-triazine has been prepared by this method, together with other products.[4] However, the method appears to be of limited generality since similar reactions of diazo-



methane with chloro di-p-tolylazirine and diazoethane with chlorodiphenylazirine gave no 1,2,3-triazines.

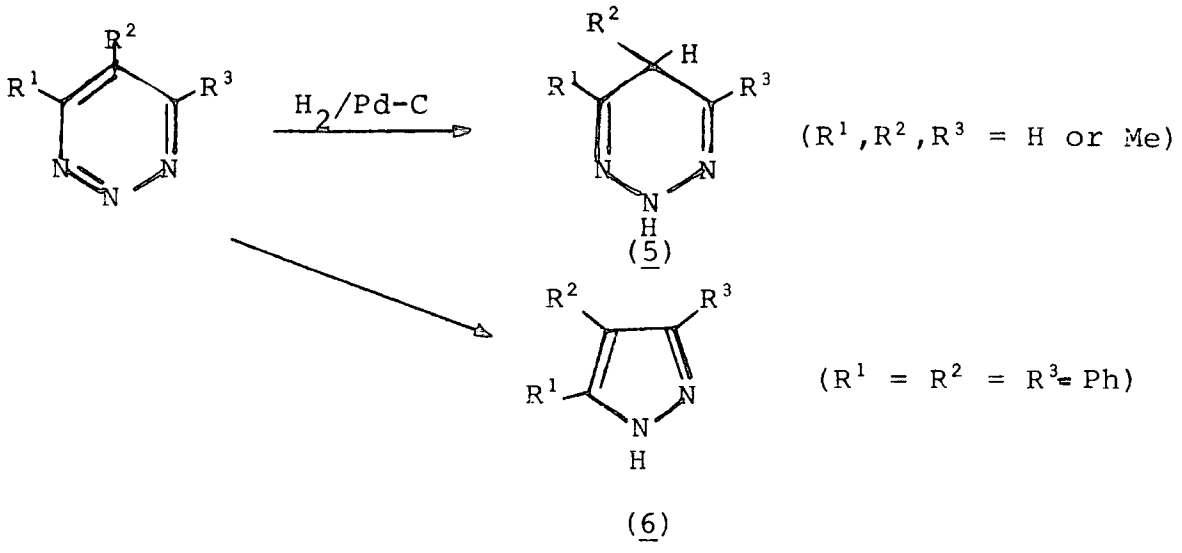
1.3 Chemistry of 1,2,3-Triazine

A few reactions of 1,2,3-triazines have been reported. they are stable to acids at room temperature but are easily hydrolyzed at higher temperatures, yielding 1,3-dicarbonyl compound (4) or products of further degradation of (4).



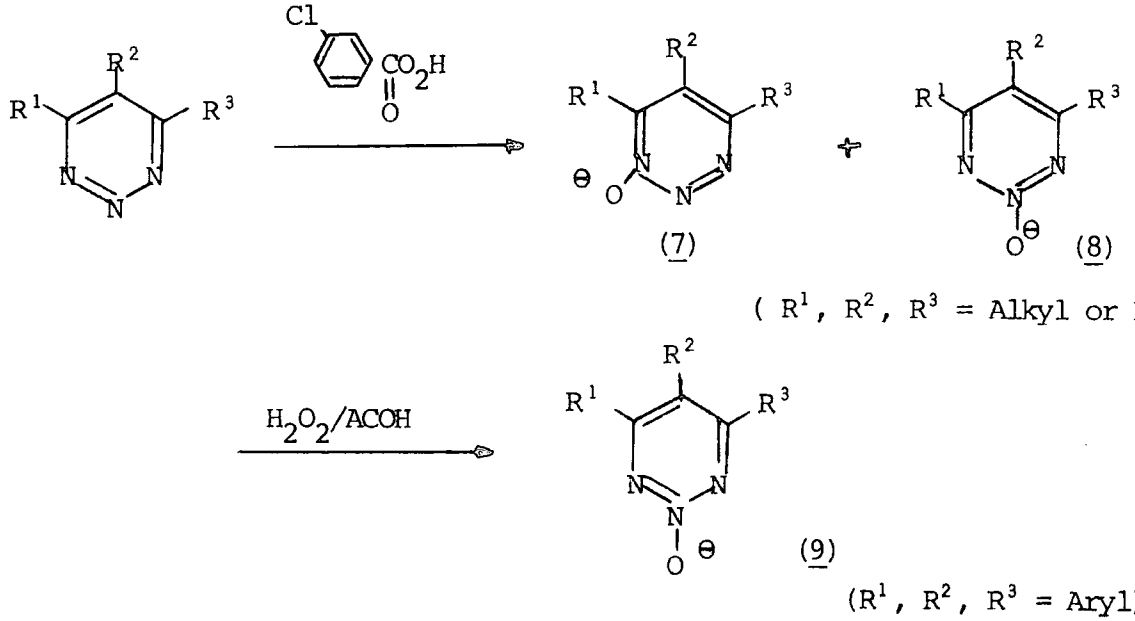
(4)

Reduction of alkyl-1,2,3-triazines with hydrogen over palladium affords the dihydro-compounds (5), while the similar reduction of triphenyl-1,2,3-triazine gives triphenyl-pyrazole (6).

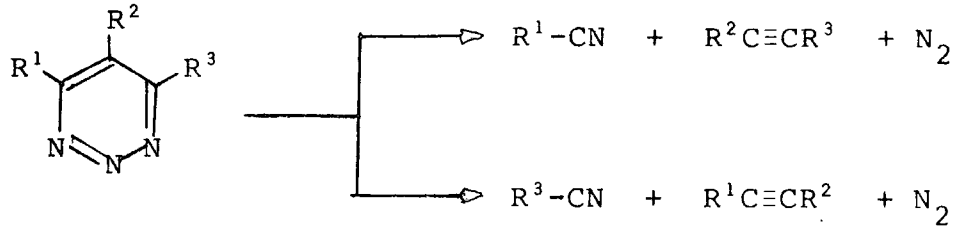


The reduction of triaryl-1,2,3-triazine with lithium aluminum hydride yields dihydro-1,2,3-triazine similar structure to (5).

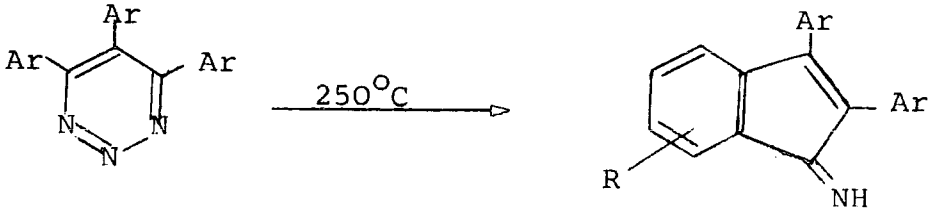
Triaryl-1,2,3-triazines can be oxidized by hydrogen peroxide in acetic acid, forming 1,2,3-triazine-1-oxides (9), while alkyl-1,2,3-triazines by m-chloroperbenzoic acid, giving a mixture of 1,2,3-triazine-1-oxides (7) and -2-oxides (8).



In most of reported photolysis of 1,2,3-triazines, an acetylene, a nitrile, and nitrogen are obtained and these fragments are also observed in the mass-spectra of these systems.

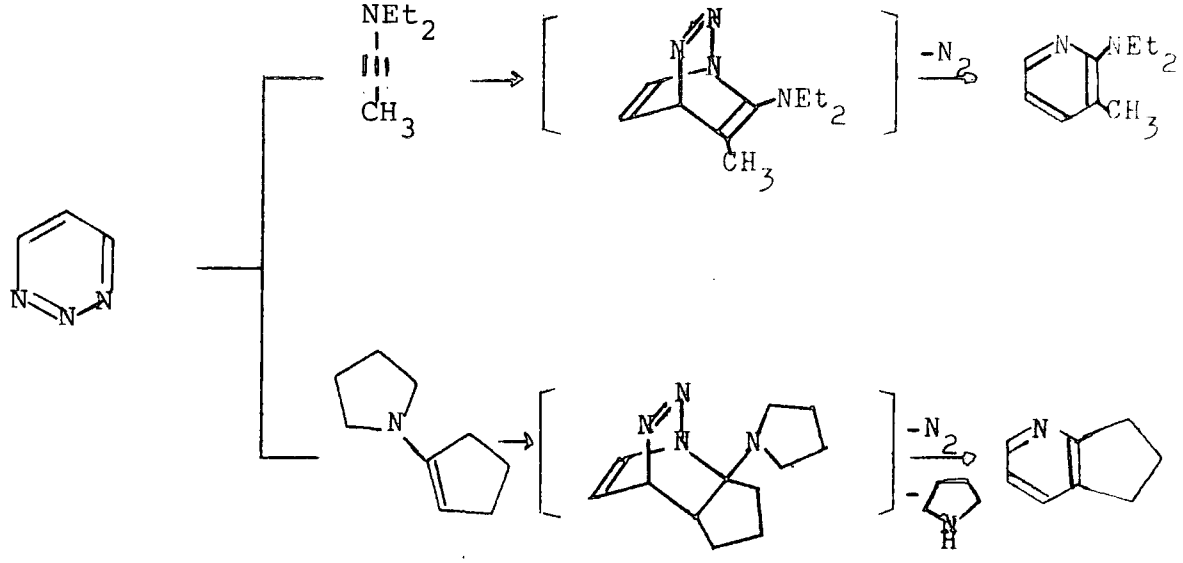


Pyrolysis of 1,2,3-triazines is the most intensively studied reaction of these systems, forming the same products as on photolysis (see Chapter Two). However, heating the 4,5,6-triaryl-1,2,3-triazine without solvent at 250°C yields mainly the indenone imines (10).[7]



(10)

Cycloaddition reaction of 1,2,3-triazine has not been reported but quoted in a review.[8] It is capable of participation in inverse electron demand Diels-Alder reactions with electron-rich dienophiles, forming pyridine derivatives.

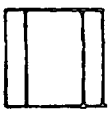


CHAPTER TWO

AZETE AND RELATED SYSTEMS

2.1 Introduction

Over the past century, antiaromatic small ring systems have continuously attracted the interest of synthetic as well as theoretical chemists. The best example is [4] annulene, or cyclobutadiene (11). Recent intensive efforts and accumulated evidence have not only led to a consistent conclusion as to several fundamental properties of (11) in the ground state but also enable us to use (11) as a versatile synthetic building-block.



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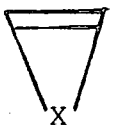


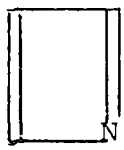
X = O, S, NR

(13) (14) (15)

In contrast, there are few reported attempts to obtain azete (12), the simplest heterocyclic analogue, which is potentially useful in synthetic chemistry. Oxirene (13) and thiirene (14) have been observed quite recently but 2-azirine (15) has not yet been identified.

2.2 Azete (Azacyclobutadiene)

Despite its similarity to the structure of cyclobutadiene, the chemistry of azete (12) remains ambiguous. Even an adduct of an unfused azete ring system has been hitherto unknown. Promising precursors are 1,2,3-triazine (16), 1,2,4-triazine (17) and oxazinone (18), which would afford (12) by the elimin-



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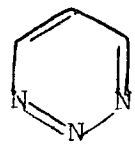

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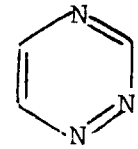

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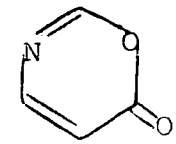


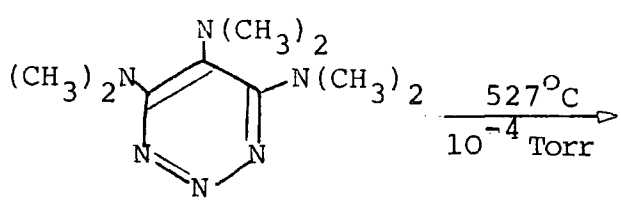
(18)

ation of nitrogen and carbon dioxide, respectively on photolysis or pyrolysis. In fact only two isolable azete derivatives have been generated from (16) though they are stabilized by benzofusion[9] or "push-pull effect", conjugative stabilization of the imine function.[10] Trichloro-[11] and alkyl-[12,13] azetes were suggested as transient intermediates *via* (17) and (18) respectively. In most of the cases so far, acetylenes and nitriles were formed as the decomposition products with no evidence of azetes. However, it is noteworthy that other precursors, triazafulvenes[14] and fluorinated pyridazine,[15] gave dimers of the corresponding azetes.

(A) 1,2,3-triazine and related systems

(i) Tris(dimethylamino)azete

Flash pyrolysis of the triazine (19) yielded the deep-red tris(dimethylamino)azete (20) in 30% yield, which was characterized spectroscopically.[10]



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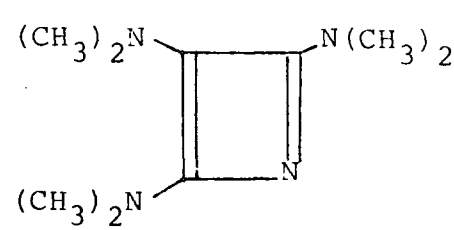
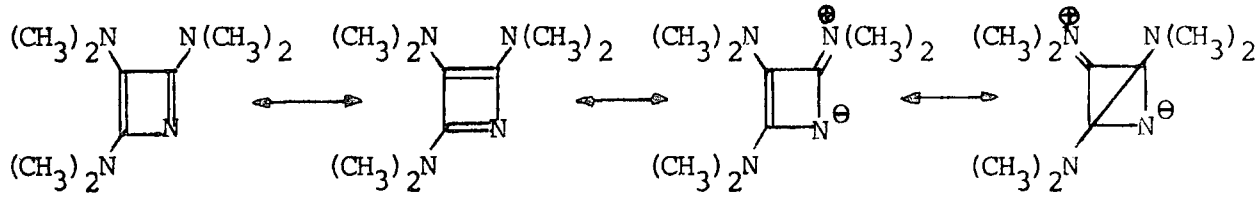


(20)

Compound (20) was stable at room temperature for *ca.* 12 hr. in solution. This remarkable stability is attributed to the resonance stabilization (20a) ↔ (20d). By analogy with the cyclobutadiene system, which was stabilized by "push-pull substitution" [see Section 2.3(C)(i)], (20) can be stabilized by two donor groups at the 2- and 4-positions, in addition to the effect of the ring nitrogen (20b and 20c).



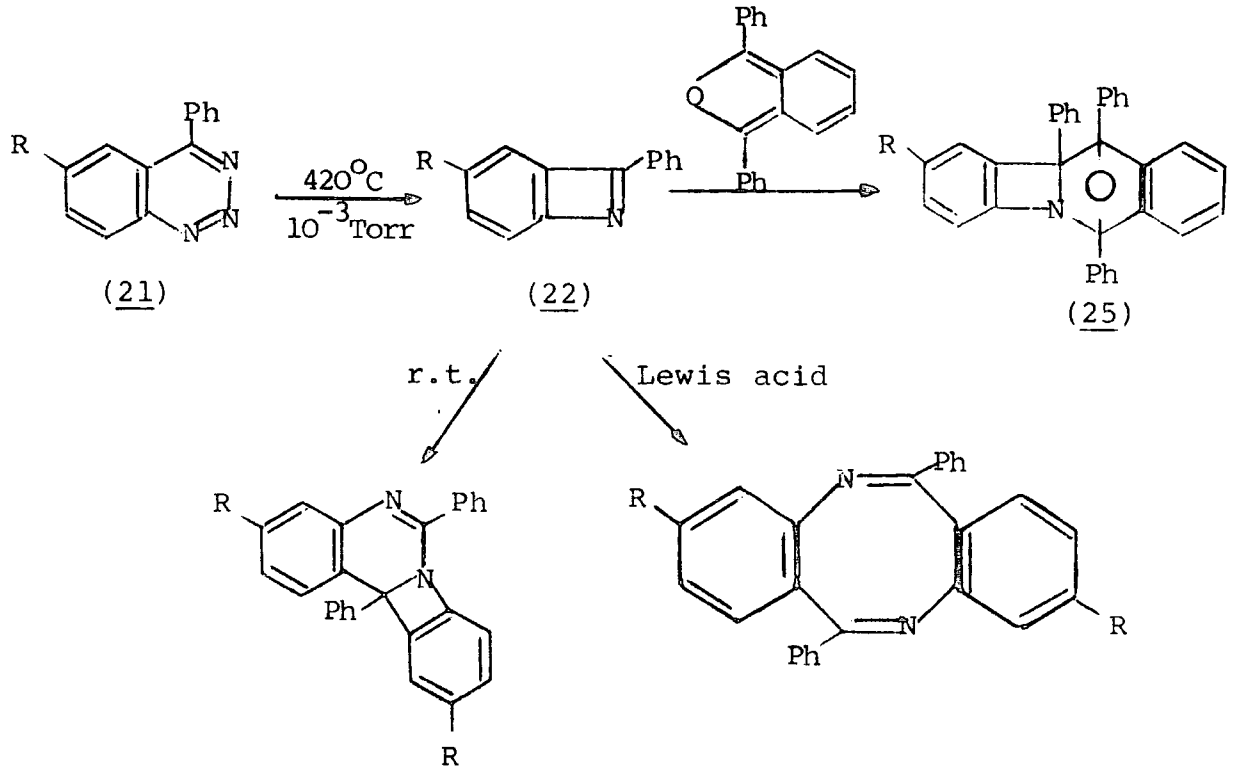
(20a) (20b) (20c) (20d)

Furthermore the transannular interaction of atoms at opposite corners of the four-membered ring (20d) is thought to compensate the destabilizing effect of a donor group at the 3-position.[16] Photo-chemical generation of (20) led to the formation of dimethyl cyanamide.

Reactions of acetylenedicarboxylic ester, isocyanate, and methyl iodide towards (20) were attempted without success.

(ii) Benzazete

2-Phenyl benzazete (22), the first reported azete, was produced by flash pyrolysis of the corresponding benzotriazine (21) in 60% yield.[9] The red product was stable up to -40°C. Derivative (22) dimerized to give an angular dimer (23) and in the presence of Lewis acid, the linear dimer (24).[17] Also, (22) is formed on photolysis and reacts with nucleophiles



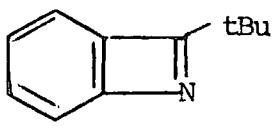
(21) (22) (25)

(23) (24)

and dienes, to give adducts such as (25), but not with dienophiles, similar to the reactivity of benzocyclobutene.[18]

2-tert-Butyl-benzazete (26) was also obtained, though in low yield (12%), in the flash pyrolysis of the benzotriazine precursor, together with isobutene (43%) benzonitrile (54%) and biphenylene (21%),[19] and gave a dimer (27) but no adducts with cyclopentadiene.

Attempted isolation of 2-methyl benzazete (28) failed, forming instead biphenylene (29) and 9-methylacridine (30).



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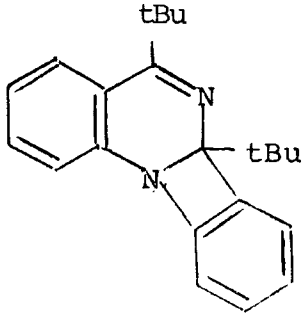

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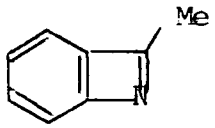

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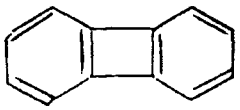

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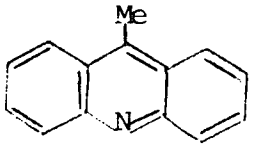
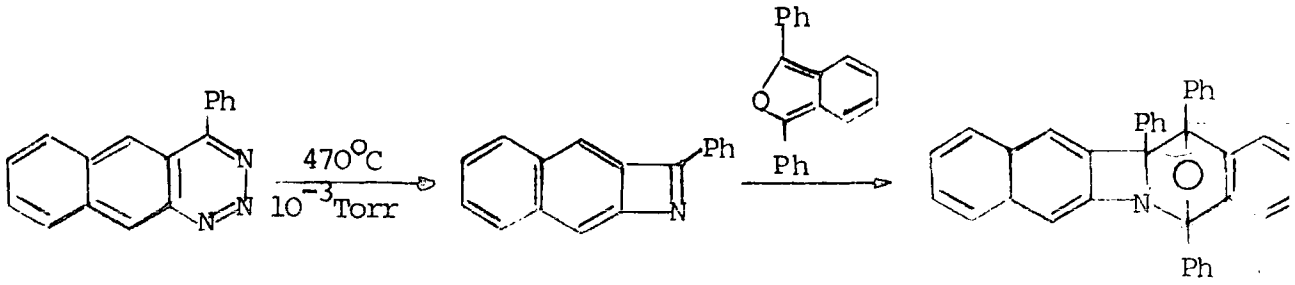


(30)

2-Phenylnaphth(2,3-b)azete (31) has been prepared and is even appreciably stable at room temperature, as an orange solid.[9] It showed reactivity towards dienes similar to (22).

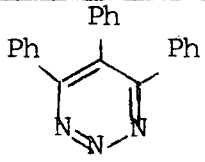
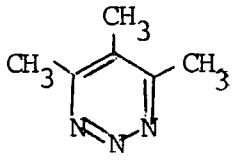
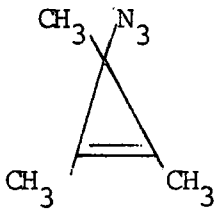
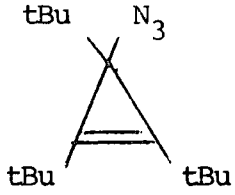
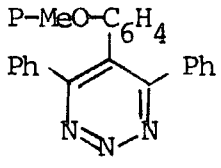


(31)

(iii) Other attempts

Other attempts to generate (12) are summarized in Table 2.1, which includes cyclopropenylazides as a precursor of (16). Obtained were the fragmentation products, without any evidence of azetes.

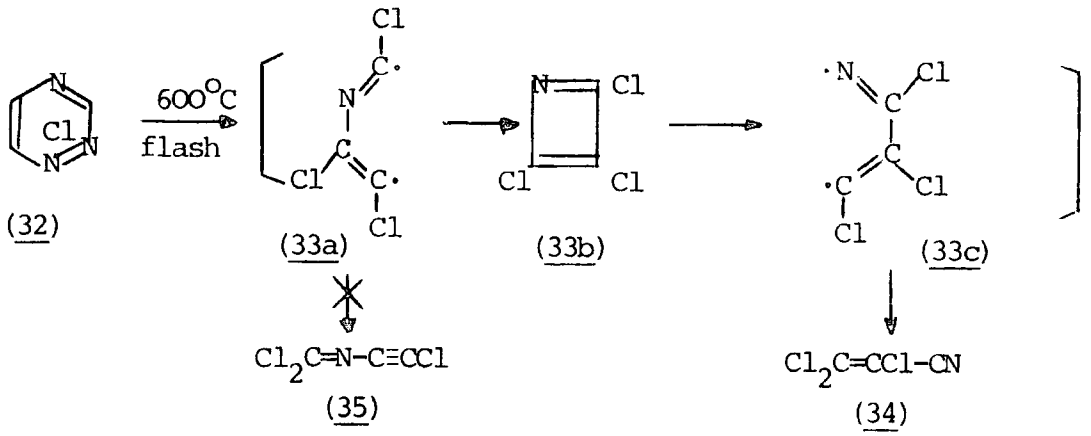
TABLE 2.1 Attempted generation of azetes from 1,2,3-triazines

Compounds	Products	Condition	Lit.
	$PhC \equiv CPh$ (72%) $PhC \equiv N$	$h\nu$ (r.t.)	20
	$CH_3C \equiv CCH_3$ (quant) CH_3CN	500°C (flow) $h\nu$ (-56°C)	21
		$h\nu$ (8KArmatrix)	12
		300°C (flow)	21
	$tBuC \equiv CtBu$ (quant) $tBuCN$	$h\nu$ (8K Ar matrix)	14
	$P\text{-}MeO\text{-}C_6H_4C \equiv CPh$ $PhCN$	625 (flash)	13

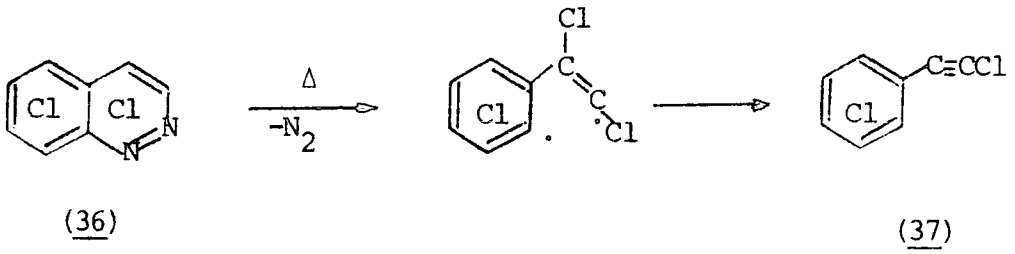
(B) 1,2,4-Triazine

(i) Trichloroazete

Trichloroazete (33b) was suggested as an intermediate when trichloroacrylonitrile (34) was yielded in the pyrolysis of trichloro-1,2,4-triazine (32).[11] Product (34)

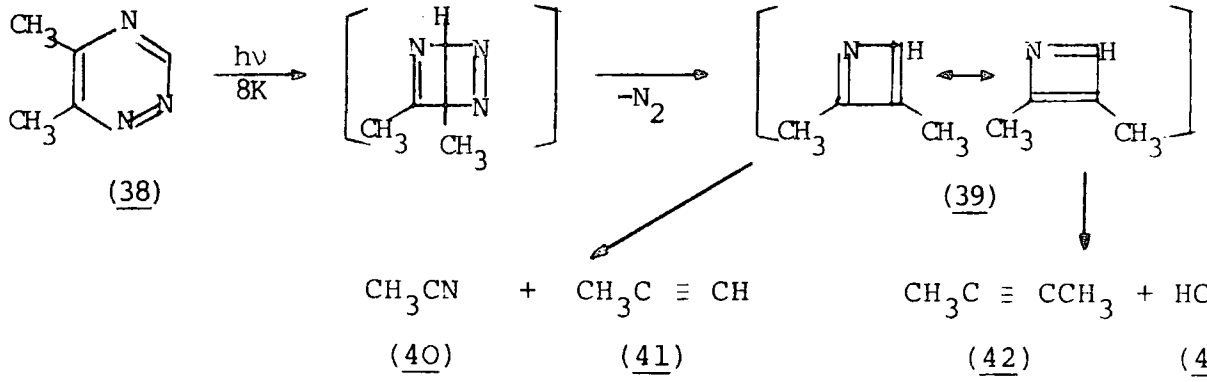


requires skeletal rearrangement arising from diradical (33a), which is most readily explained *via* formation of (33b), followed by opening to (33c). Since a product (35) was anticipated by analogy with pyrolytic formation of acetylene (37) from cinoline (36).[22]



(ii) Dimethylazete

The intermediacy of 2,3-dimethylazete (39) was deduced from the fragmentation products on photolysis of 5,6-dimethyl-1,2,4-triazine (38) in argon matrix.[12a]



(38) (39)

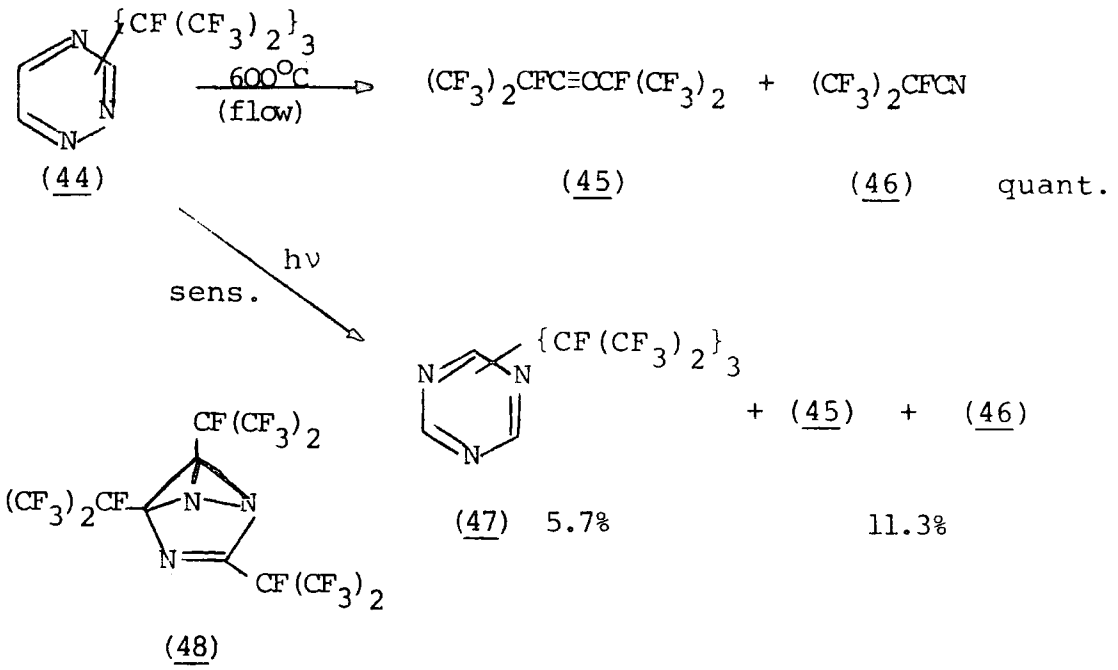
CH_3CN + $CH_3C \equiv CH$ $CH_3C \equiv CCH_3$ + HCN

(40) (41) (42) (43)

The products (40) ∿ (43) were consistent with formation of (39), following a fast valence isomerization.

(iii) Fluorinated Derivatives

Several attempts have been made to obtain fluorinated azetes without producing firm evidence of azetes. Perfluorotrisisopropyl-1,2,4-triazine (44) gave acetylene (45) and nitrile (46) on flash pyrolysis, and 1,3,5-triazine (47) together with (45) and (46) on photolysis.[11] The formation of (47) could involve triazabenzvalene (48) as an intermediate,



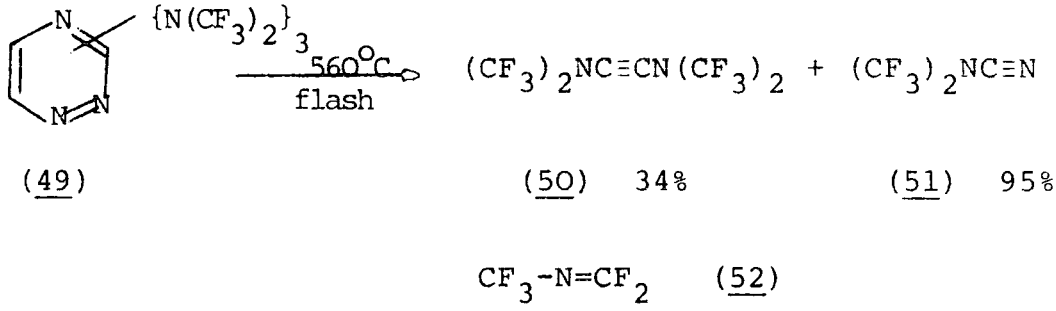
(44) (45) (46) quant.

(47) 5.7% + (45) 11.3% + (46)

(48)

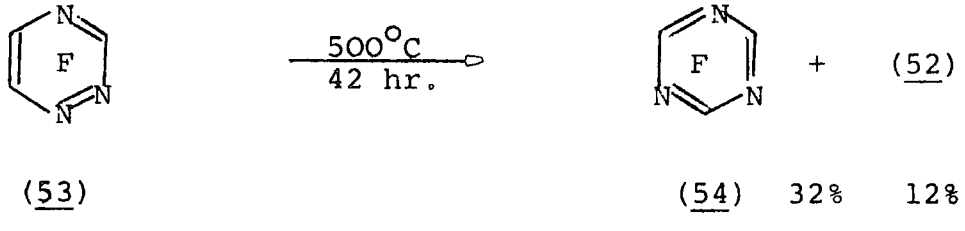
in a process which is analogous to those found in thermal rearrangement of some perfluoroalkyl pyridazines.[23]

Similar results were obtained with perfluoro-tris(dimethylamino)1,2,4-triazine (49), forming acetylene (50) and nitrile (51) on flash pyrolysis.[24] At higher temperature (620°C), the further fragmentation product, perfluoro-2-azapropene (52) also appeared.



Attempted flash pyrolysis (800°C) and photolysis of perfluoro-1,2,4-triazine (53) failed[25] but, on static pyrolysis, the triazine (53) gave 1,3,5-triazine (54) in addition to (52).

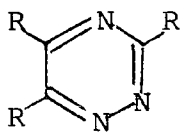
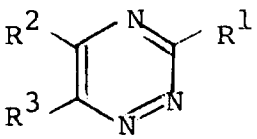
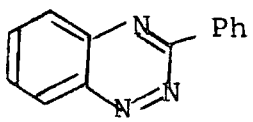
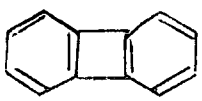
It was postulated that formation of cyanogen fluoride is involved in the process,[24] though a valence isomer could account for the results.



(iv) Other attempts

Other attempts to generate (12) are listed in Table 2.2. Acetylene, nitriles and/or other decomposition products were produced.

TABLE 2.2 Attempted generation of azetes from 1,2,4-triazines

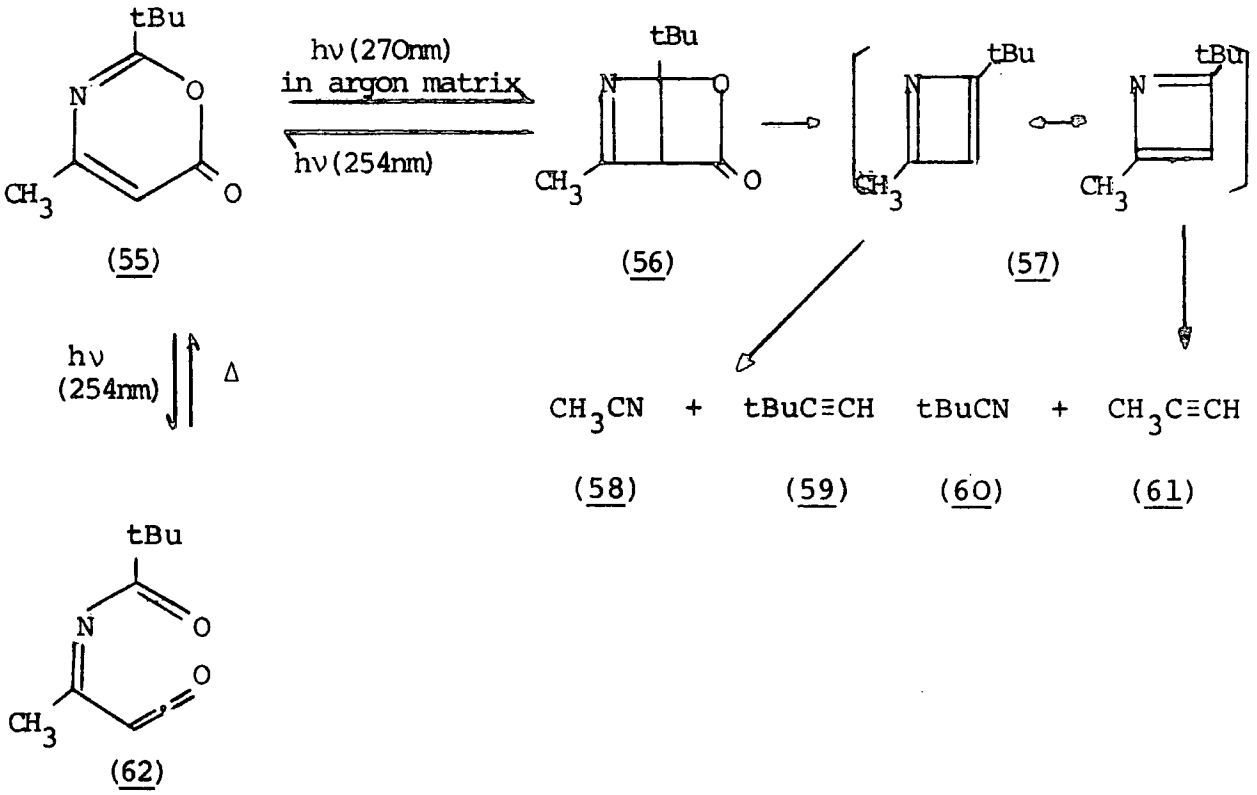
Starting material	Products (yield)	Condition	Lit.
 R = H or CH_3	R-C≡C-R (quant) R-CN	hν 8K (argon matrix)	12
	R_1CN $R_2C{\equiv}CR_3$	800°C (flash)	13
R_1=Ph, R_2=Ph, R_3=H,	76% 51%		
Ph H Ph	57% 60%		
H Ph Ph	3.5% 90%		
 Ph	 PhCN	700°C (flash)	26

(C) Oxazinone

(i) Alkyl azete

Intermediacy of alkyl azete (57) was deduced from the fragmentation products on the photolysis of oxazinone (55) *via* bicycle (56) in argon matrix or an organic glass at low temperatures.[12] Careful selection of conditions was required

since keten (62) was yielded as a by-product under certain conditions. The products suggested formation of (57) as discussed in Section (B)(ii). The product ratio (58:59):(60:61) was 6:5. Formation of the dimer of (57) was quoted without evidence.[12b] Analogous results were obtained with dimethyl oxazinones.[12b] Flash pyrolysis of (55) afforded (58), (60) and (61) in 31%, 31% and 14% respectively.[13]

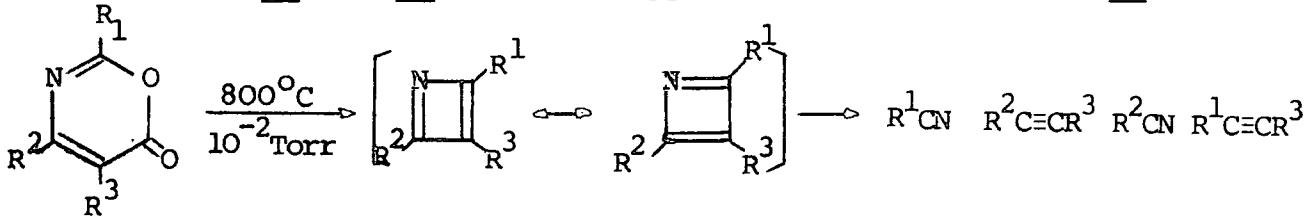


(55) (56) (57) (58) (59) (60) (61)

(62)

(ii) Arylazetes

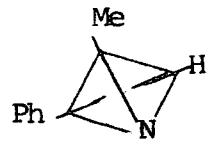
Arylazetes (64) was proposed by the distribution of products (65) ~ (68) on flash pyrolysis of oxazinones (63).[13]



(63) (64)

		(65)	(66)	(67)	(68)
(a)	R^1=P-MeOC$_6$H$_4$, R^2=R^3=Ph	12.5%	32	4.5	7.5
(b)	R^1=Ph, R^2=Me, R^3=H	14	(detected)	12	23

Furthermore, formation of an azatetrahedrane intermediate (69) was suggested, following detection of a small amount of the acetylene (70) in the case of (63b), though extreme condition sometimes leads to unusual products *via* bimolecular process.[27]



(69)

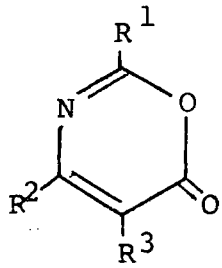
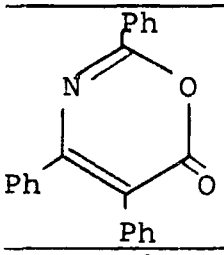
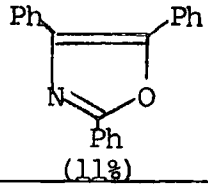
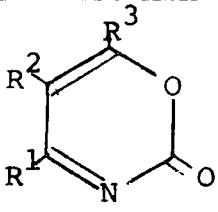
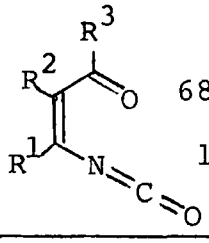
PhC≡CMe

(70) 2%

(iii) Other attempts

These are listed in Table 2.3.

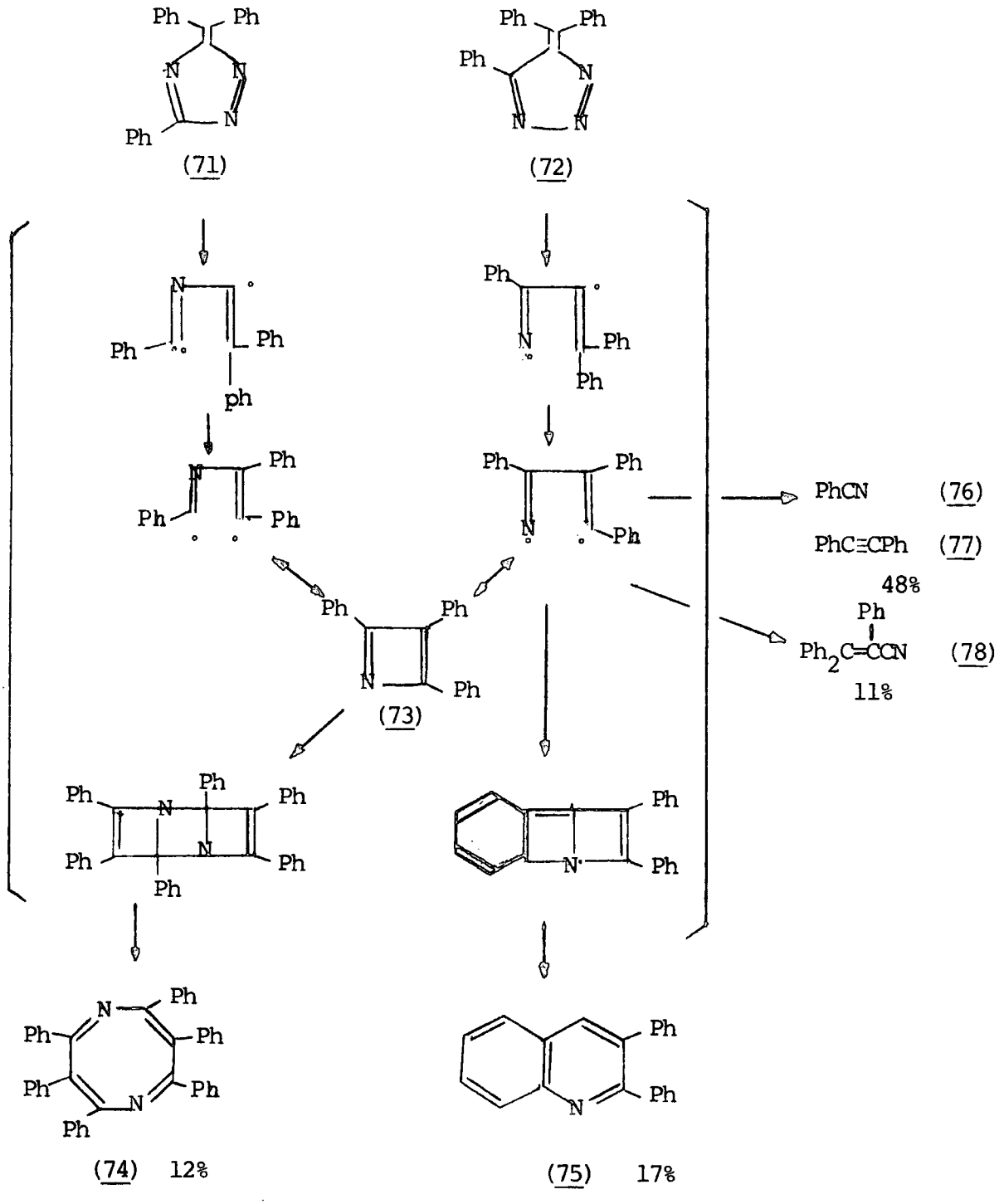
TABLE 2.3 Attempted generation of azete from oxazinones

Starting material	Products (yield)	Conditions	Lit
	(R^1=R^2=R^3=H or CH_3)	R_1CN $R_2C{\equiv}CR_3$ 8K Ar matrix or 110K organic glass	12a
	(R^1=CF_3, R^2=CH_3, R_3=H)	(not mentioned)	12b
	PhCN (45%) PhC≡CPh (42%)  (11%)	800°C 10^{-2} Torr	13
	(R^1=H, R^2=Ph, R^3=N⟨⟩O) 	680°C 10^{-2}Torr	28
	(R^1, R^2=⟨⟩, R^3=NEt_2)		

(D) Notable other systems

(i) Triphenylazete

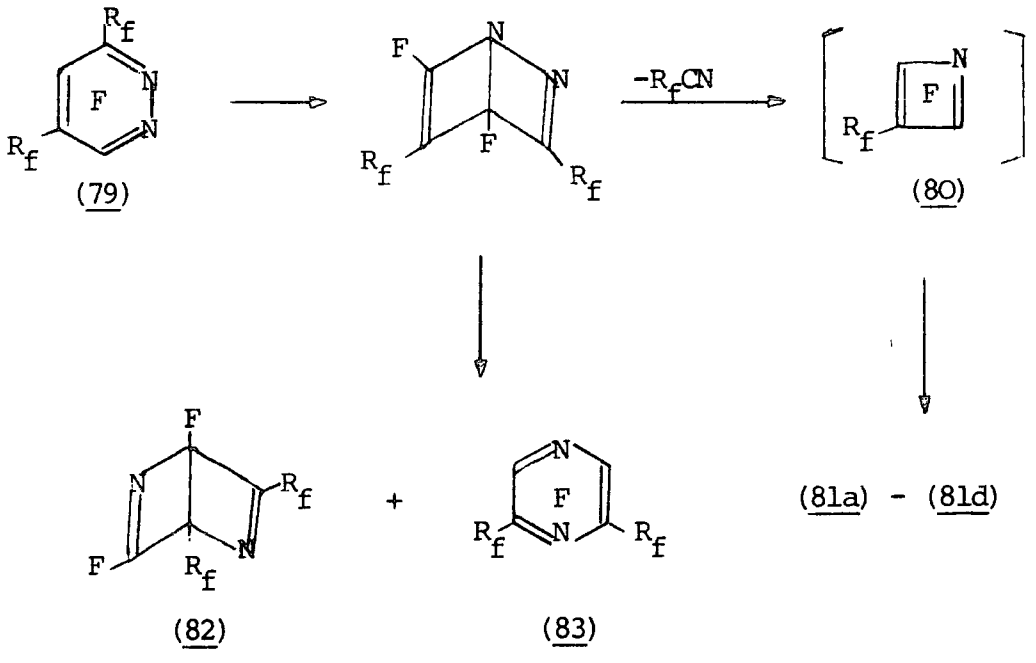
Photolysis of triazafulvenes (71) and (72) afforded diazocine (74) as well as other derivatives (75) ∿ (78), suggesting formation of the cyclic intermediate (73) especially from (71).[14]

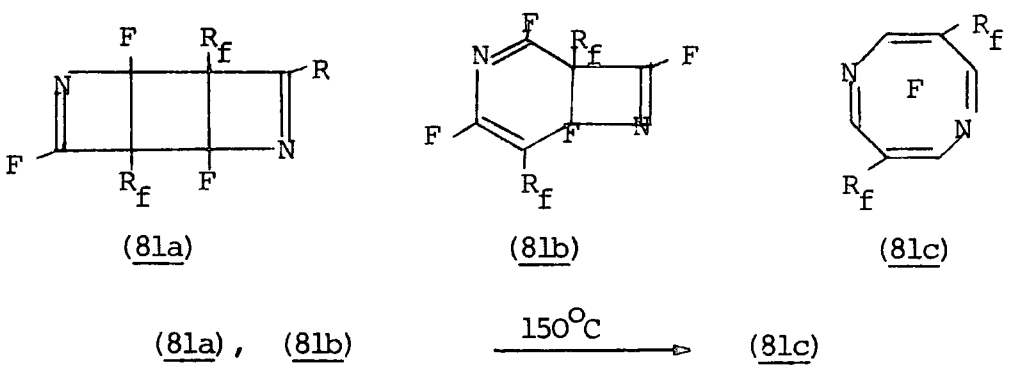


(ii) Fluorinated azete derivatives

Evidence for the generation of fluorinated azete (80) was obtained when perfluoro-3,5-diisopropyl-pyridazine (79) was photolyzed in a flow system.[11]

Produced were four dimers of the cyclic intermediate (81a) ∿ (81d), together with rearrangement products (82) and (83). Dimers (81a) and (81b) were found to undergo ring opening reaction to the 1,4-diazocine (81c) on heating.

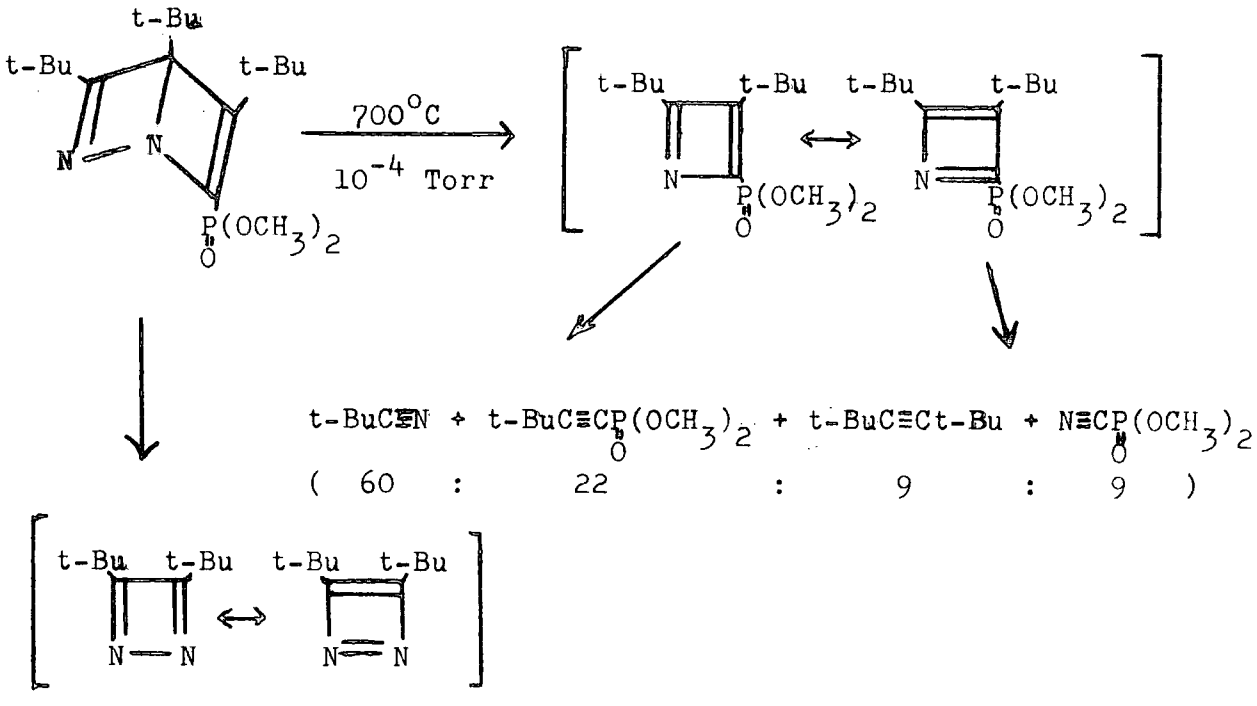




(81a), (81b) $\xrightarrow{150^{\circ}C}$ (81c)

(iii) Phosphoryl azete

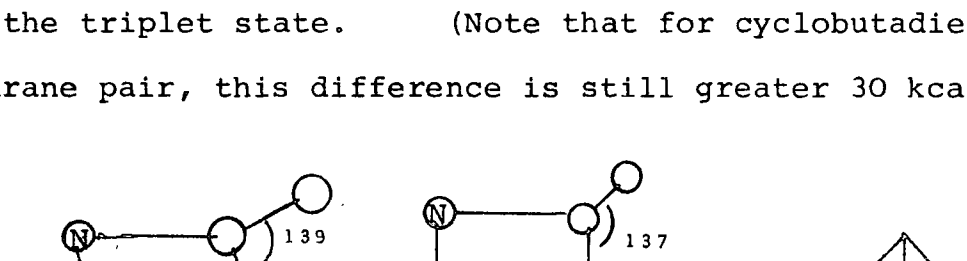
An intermediacy of a phosphorylazete has been reported quite recently.[263] A 1,2-Dewarpyridazine gave the fragmentation products on flash pyrolysis, which are more consistent with the azete than a 1,2-diazacyclobutadiene intermediate. Since the latter could not account for the phosphorylnitrile.



(E) Theoretical aspects

A negative resonance energy of 15.5 kcal/mole was calculated for azete.[29] This is somewhat less than the corresponding value for cyclobutadiene of 18 kcal/mole[30] and demonstrates the antiaromatic character of these compounds, and the stabilizing effect of the nitrogen atom.[31] This view was supported by recent more elaborate calculations.[32,33]

Electronic and spatial structure of azete have been reported recently,[34] showing that azete has a ground singlet (So) state and its spatial configuration has the form of a slightly distorted rectangle (84) [*N.B.* 2.3 (D)(ii)]. The first excited triple (T1) state lies 9 kcal/mole higher than the So state and in this state azete has the form of a slightly distorted square (85). Furthermore, the valence isomer, azatetrahedrane (86) does correspond to a minimum in potential energy surface of C_3H_3N, 19.5 kcal/mole higher energy than So but has no stability in the triplet state. (Note that for cyclobutadiene-tetrahedrane pair, this difference is still greater 30 kcal/mole).



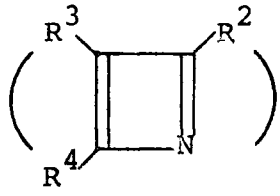
S_o (84) T_1 (85) (86)

Resonance energies of azetes with various substituents (Table 2.4) clearly shows significant stabilizing effect of fluorine at the 2- and 4-position,[35] *i.e.*, 2,4-difluoro azete could have positive resonance energy and the effect is larger than amino group, while the destabilizing effect at the 3-

position is less than that of amino-group. This result is in accord with the known electron-donating ability of fluorine bonded to electron-demanding sites.[37,38,39]

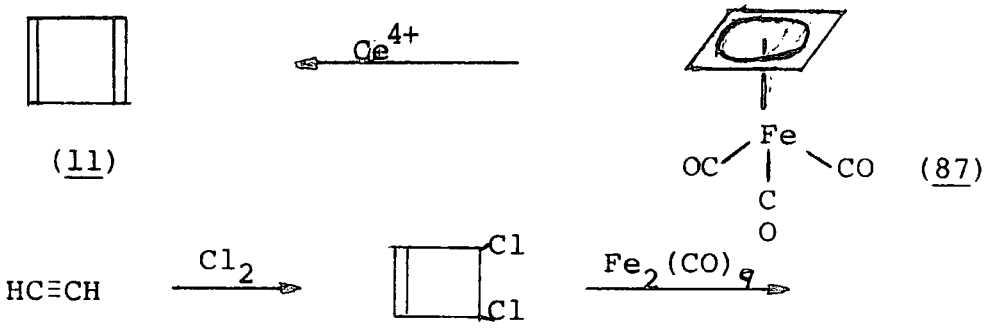
TABLE 2.4 Resonance Energies in Unit of β for Azete.[35]

Substituents			Resonance Energies (β unit)	Other method[36]
R^2	R^3	R^4		
H	H	H	- 0.64	- 0.77
H	NH_2	H	- 0.76	- 0.58
NH_2	H	NH_2	- 0.26	- 0.22
NH_2	NH_2	NH_2	- 0.46	- 0.20
F	H	H	- 0.18	- 0.28
H	F	H	- 0.69	- 0.52
F	H	F	+ 0.05	- 0.13

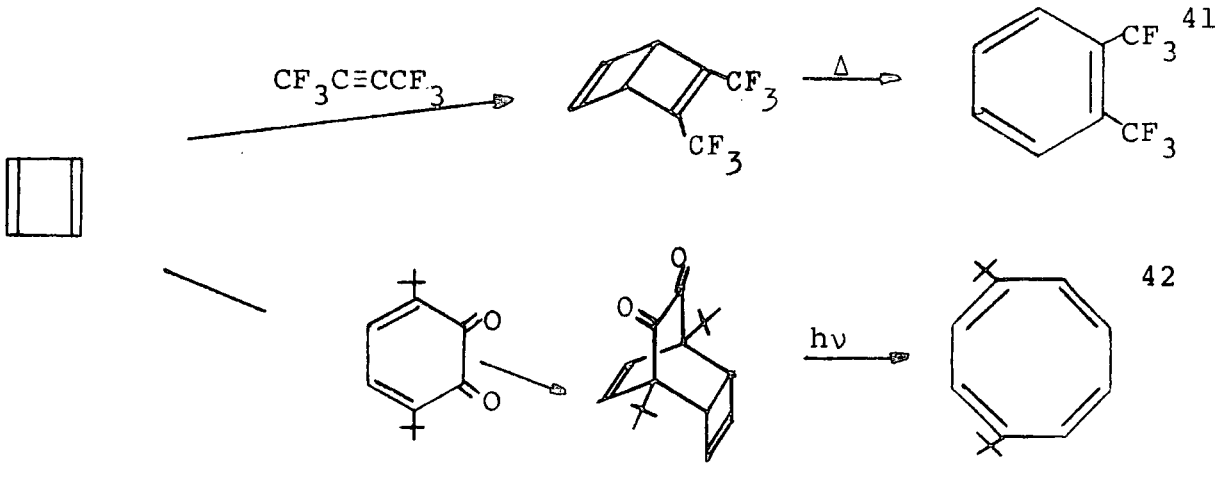


2.3 Cyclobutadiene

Accumulated evidence by 1967 demonstrated clearly that cyclobutadiene (11) undergoes dimerization and other intermolecular reactions with extraordinary ease.[18] Its apparent stability with respect to decomposition and rearrangement renders it a versatile synthetic building-block, partly by the development of iron-carbonyl complex (87).[40]



Cyclobutadiene (11) behaves both as a dienophile and a diene in Diels-Alder reactions, giving endo-adducts, usually through a concerted process.



During the last decade, several approaches have been made to obtain stable monocyclic derivatives.[43,44] These are discussed as follows:

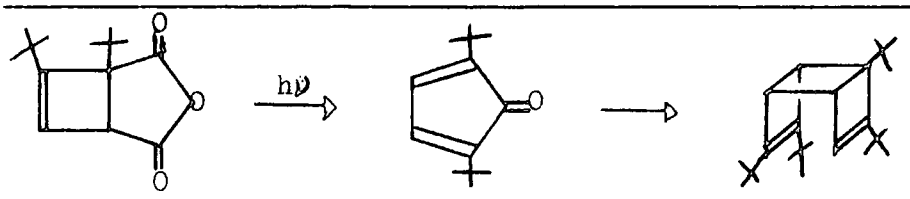
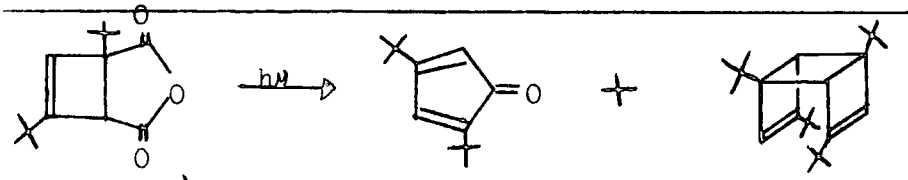
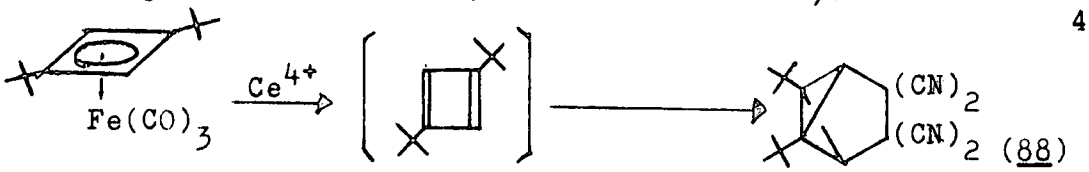
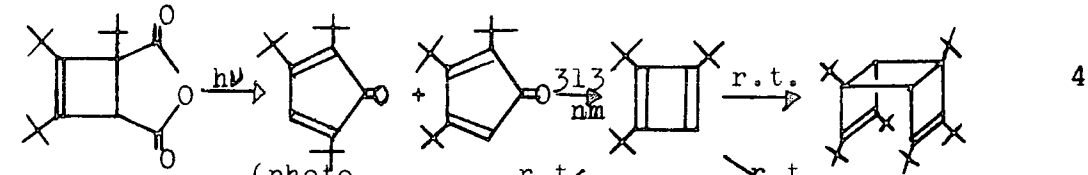
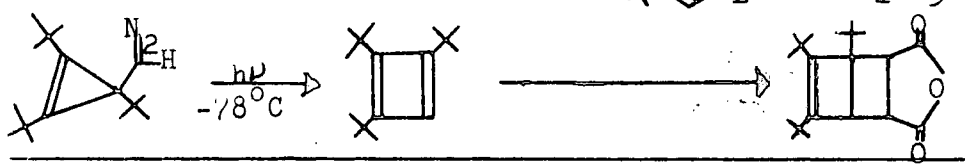
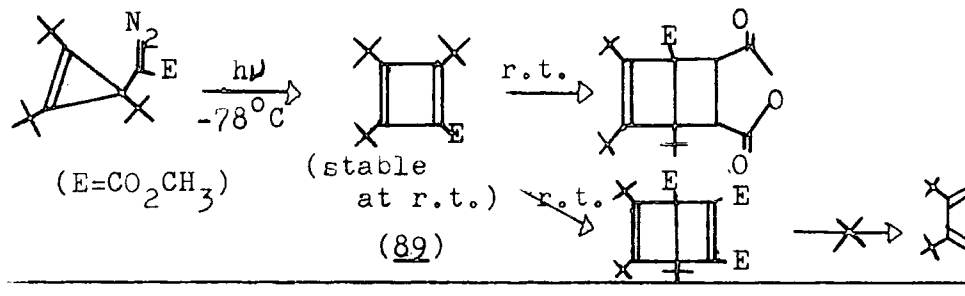
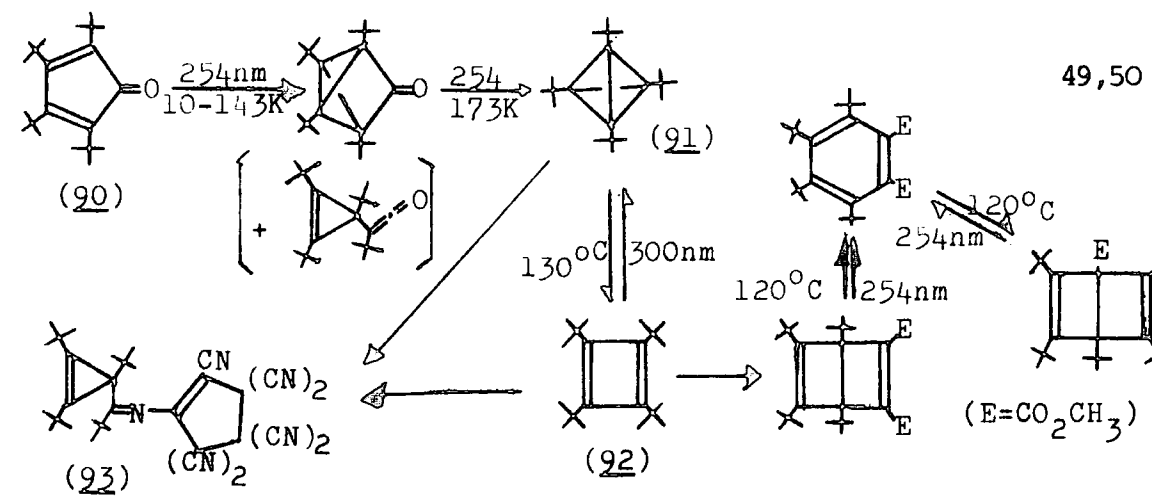
(A) Alkyl substituted derivatives

tert-Butyl derivatives (see Table 2.5) have been extensively studied since a methyl group was found not to be bulky enough to block dimerization.[44] In most cases, the cyclobutadiene derivatives were generated by photoelimination reactions at low temperature. Higher substitution led to more stable derivatives and eventually tetra-substituted derivatives (89)

proved to be stable at room temperature. It is noteworthy that the primary product on photolysis of tetra-tert-butyl cyclopentanone (90) under appropriate conditions turned out to be the first derivative of long-sought tetrahedrane (91). The highly strained (91) rearranges to the originally sought cyclobutadiene (92) on warming to 130°C. This stability is understood kinetically.

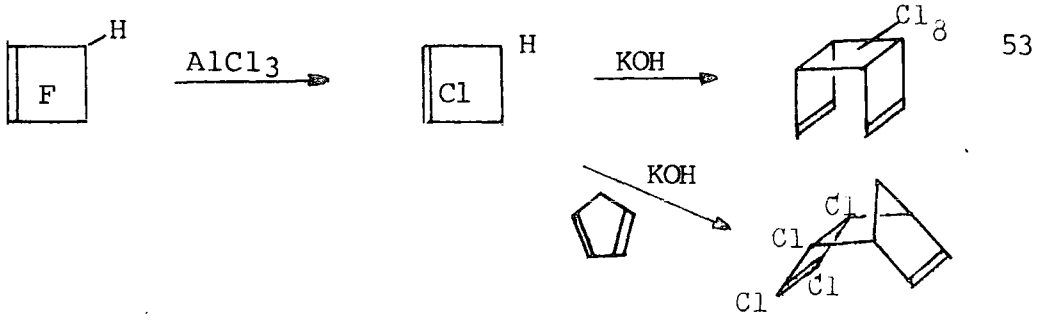
Most of cyclobutadienes react with dienophiles to yield Diels-Alder adducts. However, with tetracyanoethylene obtained were some unusual products such as (88) and (93). It would be more straightforward to assume the intermediacy of zwitterionic species,[50] also observed in other special cases,[51,52] although (88) can, in principle, be explained in terms of a concerted [2+2+2] cycloaddition.[46]

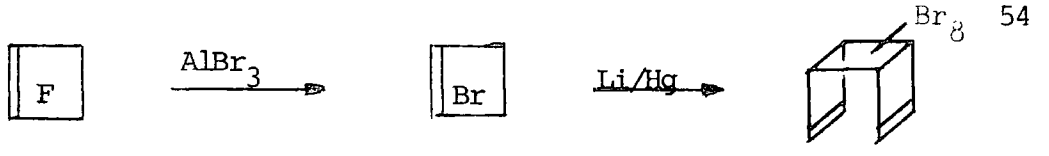
TABLE 2.5 t-Butyl cyclobutadienes and their derivatives

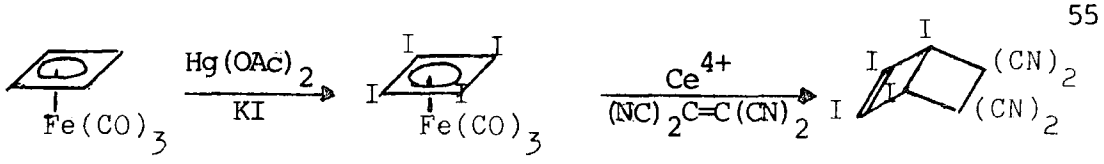
Starting Material	Product and Condition	Derivatives	Lit.
			45
			45
			46
			47
			48
			48
			49,50

(B) Halogenated derivatives

Partially chloro- and bromo-substituted derivatives are referred to in an early book on cyclobutadiene.[18] However dimers of perchloro- and perbromo-derivatives were obtained later[53,54] from analogous starting materials, *i.e.* fluorinated cyclobutenes. An iodo-derivative was reported to give an adduct with tetracyanoethylene[55] without further investigation.





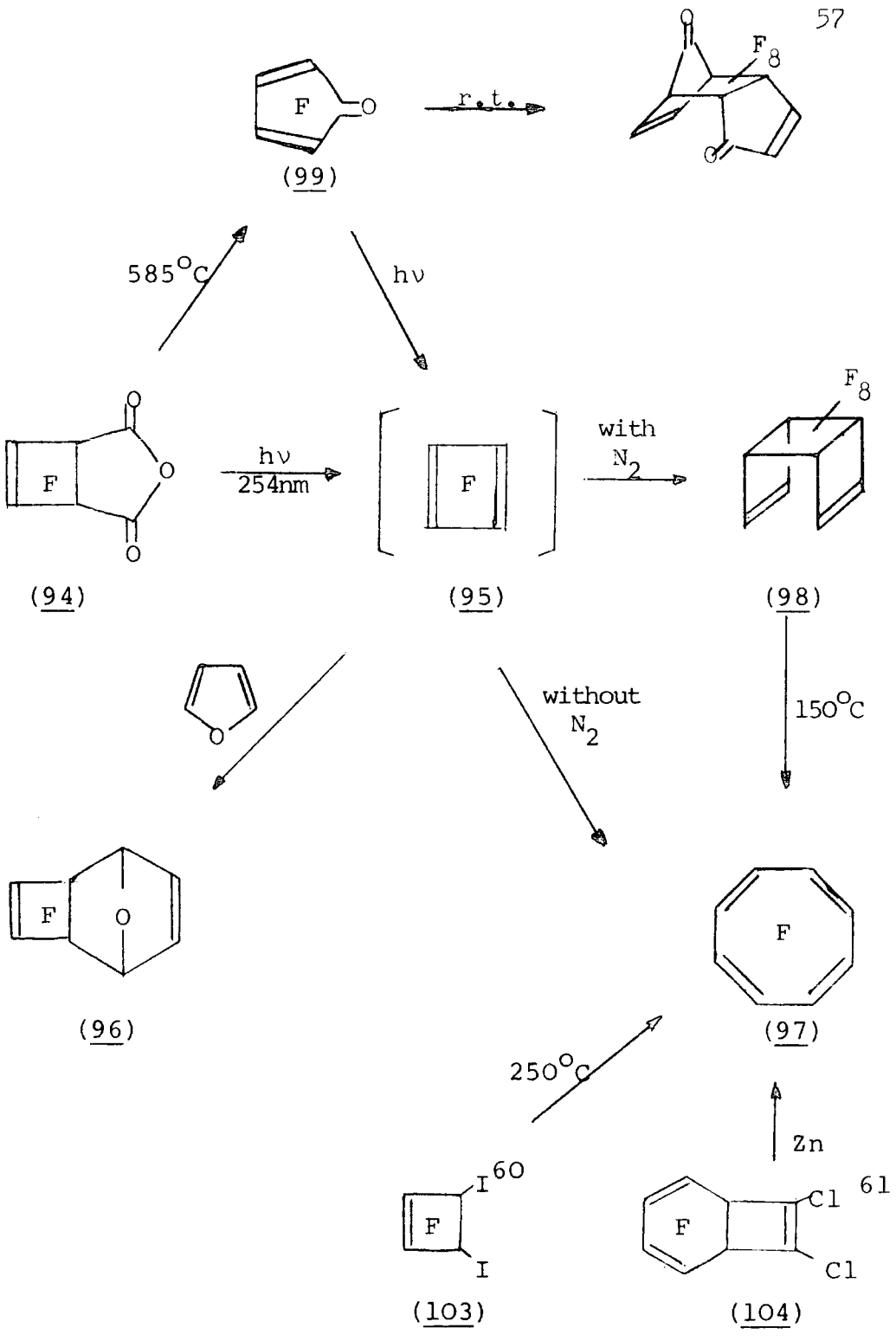


In contrast fluorinated derivatives have been fully investigated to the point of chemical reactions of dimers, which are discussed in detail.

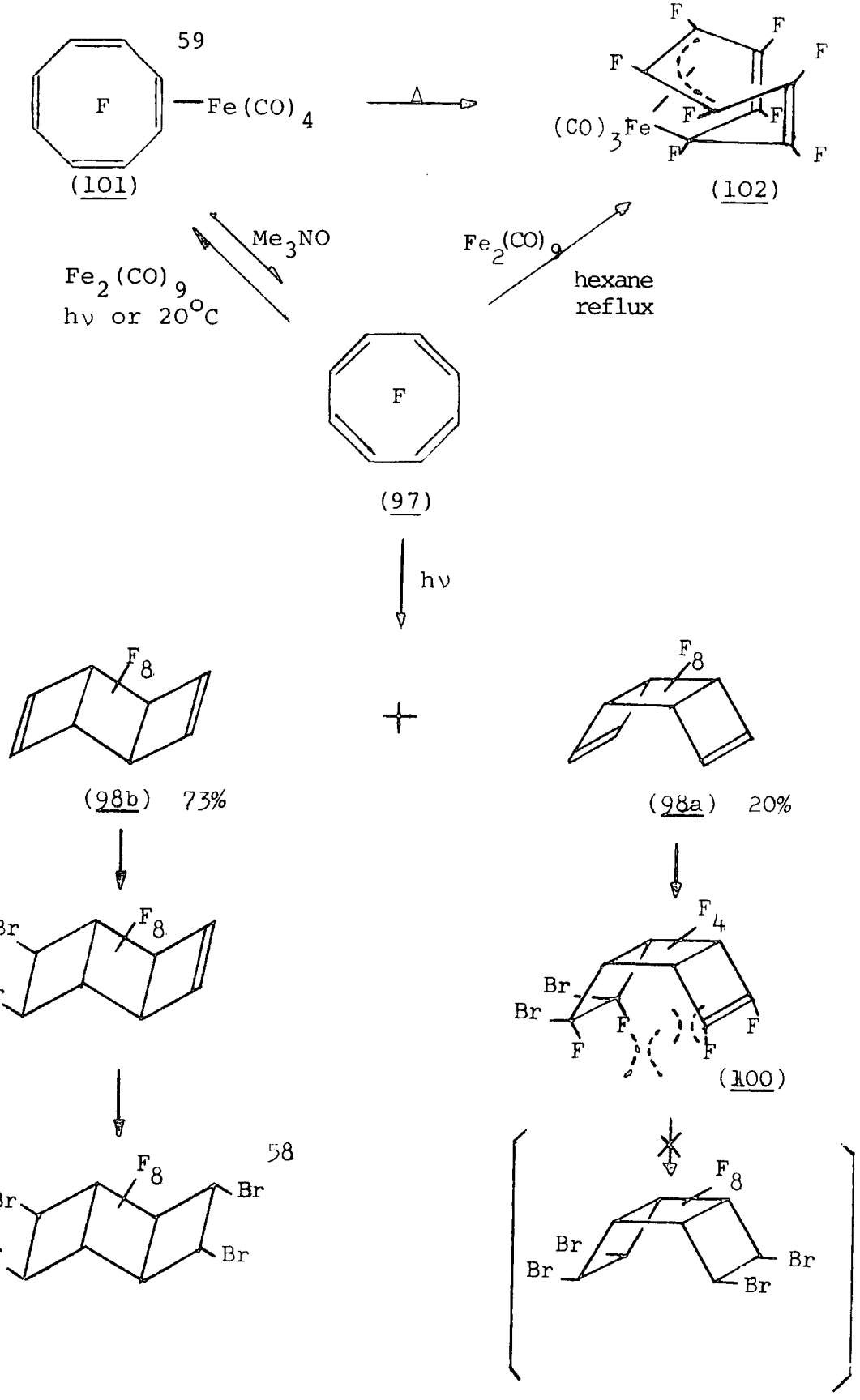
(i) Perfluoro-cyclobutadiene

Evidence was advanced for the intermediacy of perfluorocyclobutadiene (95) , generated by photolysis of anhydride (94)[56] as shown in Scheme 2.1. The cyclobutadiene (95) was trapped by furan to form an adduct (96) but not by dienophiles such as ethylene and perfluorocyclobutene. The only isolable

Scheme 2.1 Perfluorocyclobutadiene and its derivatives



Scheme 2.1 (continued)



products were cyclooctatetraene (97) and its tricyclic isomer (98) without dienes. The isomer (98) was converted to (97) on warming up to 150°C.

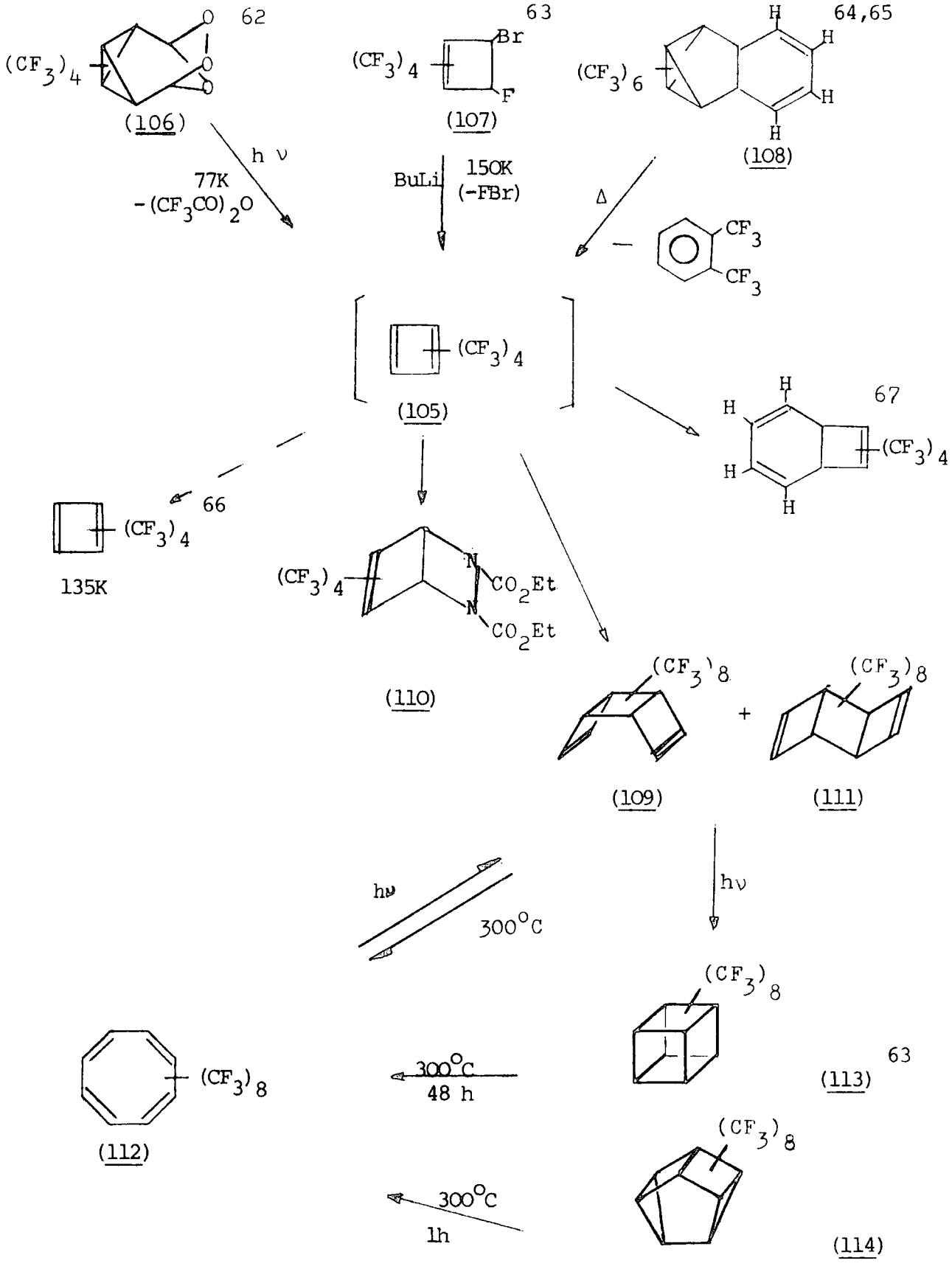
Perfluorocyclooctatetraene (97) was obtained *via* pentadienone (99),[57] and underwent photo-ring closure to a mixture of endo- and exo-tricyclic isomer [(98a) and (98b) respectively], which added bromine exclusively in the exo, suprafacial fashion, but only the isomer (98b) added two moles of bromine. This was attributable to nonbonding interaction between fluorines in (100). In fact F-F coupling (J = 25Hz) through space was observed.[58]

Another remarkable feature of (97) was revealed when it afforded η^2complex (101), the second example of this sort, with transition metals, which was converted to η^4 complex (102) with σ-bond (an oxidative addition product).[59] Formation of (97) has been reported from other precursors (103)[60] and (104)[61] recently.

(ii) Tetrakis(trifluoromethyl)cyclobutadiene

This novel species (105) was reported at the same time but independently by three groups, as shown in Scheme 2.2.[62,63,64] Precursors are an ozonide (106),[62] a cyclobutene (107),[63] and a decadiene (108).[64,65] The irradiation of (106) in organic glass at 77K yielded a yellow coloured photolysate, which provided white crystals (109) upon thawing the matrix. The photolysate formed an adduct (110) with ethyl diazodicarboxylate, a very strong dienophile. The dimer (109) was obtained by flash pyrolysis of (108), clearly indicating the same intermediate (105).[64,65] Subsequently, the monomeric species was observed and subjected to extensive spectral characterization as the

Scheme 2.2 Tetrakis(trifluoromethyl)cyclobutadiene and its derivatives



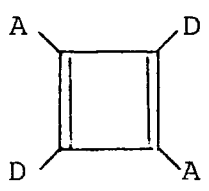
first symmetrically substituted cyclobutadiene by a different group.[66]

Species (105) was also afforded by the elimination of LiF from (107) *via* an unstable lithium compound, giving syn- and anti-dimers [(109) and (111) respectively].[63] When heated to 300°C, they isomerized to the thermally very stable, but photochemically labile, cyclo-octatetraene (112). Irradiation of (112) yielded initially a complex mixture, including (109) and (111), but finally saturated valence isomers cubane (113) and cuneane (114).[63] They were very stable too but reverted to (112) thermally at 300°C.

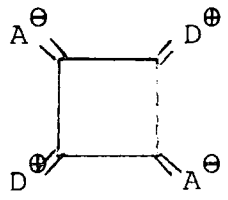
(C) Notable other systems

(i) Push-pull systems

It had been postulated that cyclobutadiene could be stabilized with substituents D(electron-donor) and A(electron-acceptor) at symmetrical positions such as in resonance form (116).[68,18] This view was confirmed when (118) was synthesized

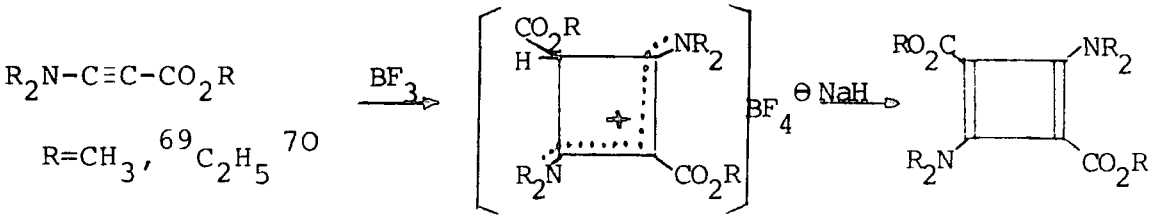


(115)



(116)

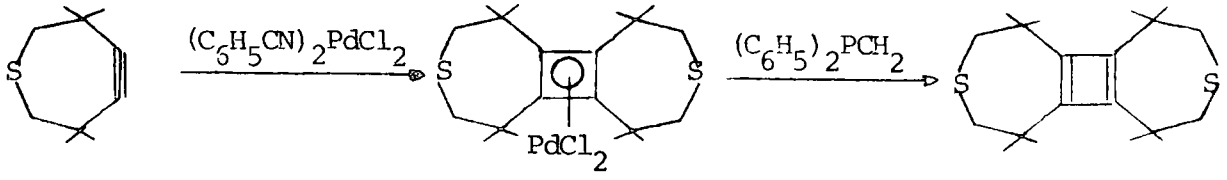
by two groups independently from ynamine (117) as the first stable cyclobutadiene[69,70] at room temperature although it could not be electronically intact.



(117) (118)

(ii) Ring-system

Thermal dimerization of strained cycloalkynes represents another entry to stabilized cyclobutadienes. Though cyclohexynes remained unsuccessful,[71] (119) provided the Pd(II) complex (120), which upon ligand exchange afforded the first isolable crystalline derivative (121).[72] It formed a Diels-Alder adduct with dimethyl acetylenedicarboxylate.



(119) (120) (121)

The photo-electron spectrum showed that no transannular n/π interaction exists between sulphur and the ring.

(D) Theoretical aspects and matrix isolation of the parent compound

(i) Theoretical aspects

It was early recognized that (11) presented a unique problem in quantum chemistry and that it was not properly tractable within a one-electron MO or a simple VB approximation.[18]

With regard to the geometry and multiplicity of ground-state (11) in different conformations, three main possibilities had emerged, which are visualized in diagrams A, B and C of Fig. 2.1(b), which depict a section through the C_4H_4-hyper-surface along a (hypothetical) reaction coordinate of inter-connecting two identical rectangular forms of (11) *via* a square (Figure 2.1(a)).

All calculations agreed with the qualitative expectation that (11) in its lowest singlet state should possess a rect-angular equilibrium geometry. In contrast, the relative energy of the lowest singlet (SS) and triplet state (ST) at square geometries was an issue of controversy.[43] Eventually recent three most elaborate calculations available have predicted that SS lies 7.3∿13.9 kcal/mole above ST which, in turn, is 8.3∿13.4 kcal/mole above RS (potential surface B).[73]

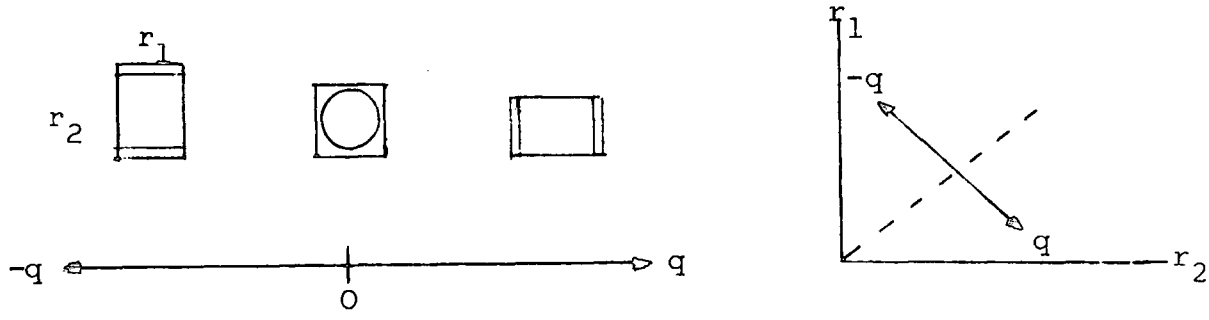


Figure 2.1(a) Definition of a (hypothetical) reaction co-ordinate linking the two rectangular forms of (11)

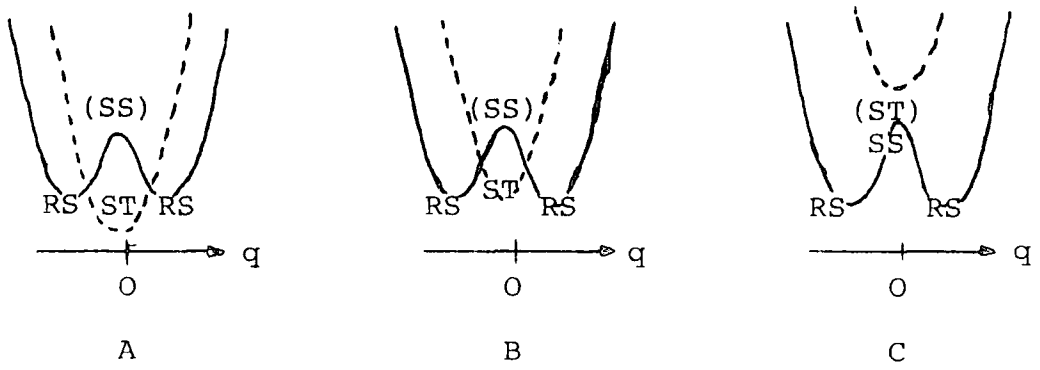
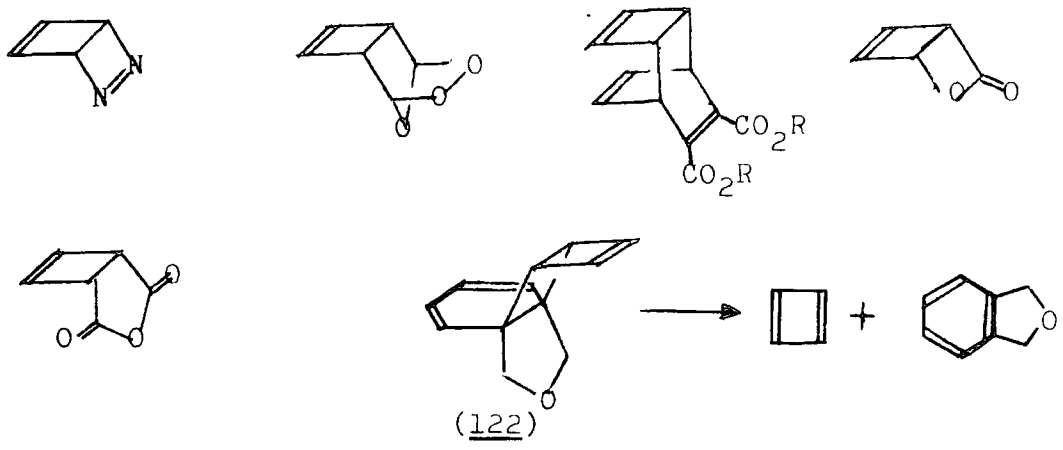


Figure 2.1(b) Possible potential surfaces for the interconversion of two forms of (11). Definition RS: Rectangular Singlet, SS: Square Singlet, and ST: Square Triplet. Abbreviations without brackets refer to the ground state, those in brackets to excited state

(ii) Matrix isolation of the parent compound

The short-lifetime of (11) as a monomeric species in gas phase as well as in solution (10 ms at 35 Torr)[76] precluded the conventional spectroscopic methods. But matrix isolation[75] could be applied, since it has been developed for characterization of reactive or unstable species detained in a suitable host material at low temperatures

Various types of possible precursors were synthesized to satisfy the requirements in order to serve as a useful source of (11) at cryogenic conditions. They are shown below.[43]



However, some of them were found not to meet the criteria for matrix isolation in stability or absorption of co-fragments. Eventually photochemical generation of (11) from (122) has led to observation of clear IR spectrum,[76] which is in good agreement with calculated frequencies and relative intensities of IR-active vibrations,[77] concluding that the geometry of the ground state is rectangular singlet (D2h symmetry).

This result is also in accord with X-ray crystallographic analyses of sterically stabilized cyclobutadienes.[43]

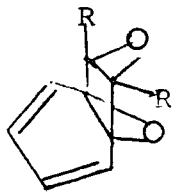
2.4 Oxirene, Thiirene and 2-Azirine

These three-membered ring analogues are systems under the combined stress of ring strain and electronic destabilization[78] and were postulated as reactive intermediates.[79]

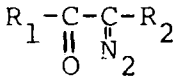
(A) Oxirene

Evidence for their transient existence was obtained in the photochemical Wolff rearrangement of α-diazo ketones[80,81] and since then they have been shown to occur as reactive intermediates in several other reactions.[78,82] Matrix isolation techniques have been applied for the characterization of this elusive species (13).

An attempt using precursors (123) to generate oxirene by retro-Diels-Alder reaction failed.[83] Also several α-diazo ketons with various substituents (124) gave ketene derivations on photolysis at 10K.[83] However, perfluoro-alkyl α-diazo ketons



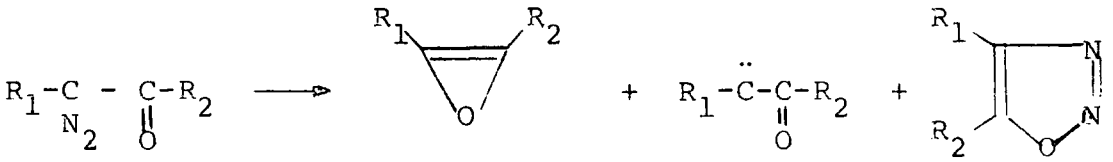
(123) R = H or CH_3



(124)

R_1;	H	tBu	CH_3	C_2F_5	CF_3
R_2;	H	H	CH_3	H	CO_2CH_3

(125) have given oxirene derivatives (126), together with keto-carbene (127) and oxadiazole (128), on photolysis under similar conditions to (124), though oxirene (126) is not stable at 35K.[84]



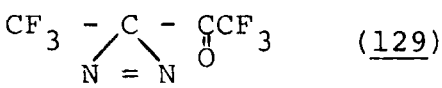
(125) (126) (127) (128)

(a) $R_1 = R_2 = CF_3$

(b) $R_1 = CF_3$, $R_2 = C_2F_5$

(c) $R_1 = C_2F_5$, $R_1 = CF_3$

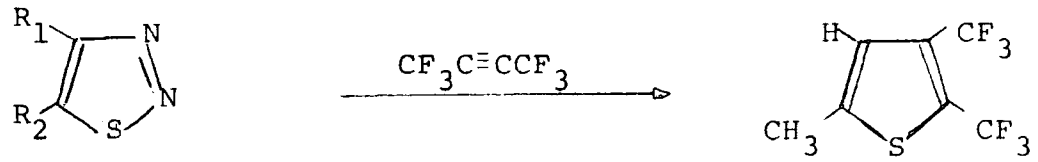
The IR spectra are in reasonable agreement with the theoretically calculated spectrum.[85] No attempt has been made to trap the species.[93] More recently (127a) has been identified to be a different species, the diazirene (129) by another group.[92]



(129)

(B) Thiirene

The intermediacy of thiirene was suggested when 4- and 5-methyl-1,2,3-thiazoles (130) gave the same adduct, 5-methyl-2,3-bis(trifluoromethyl)thiophene (131) with hexafluorobut-2-yne

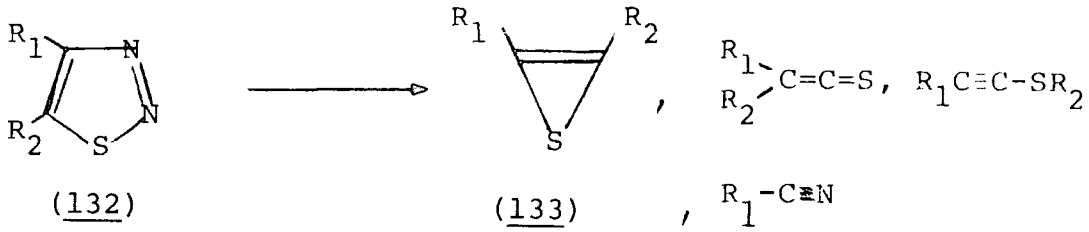


(130) (131)

(a) R_1 = H, R_2 = CH_3

(b) R_1 = CH_3, R_2 = H

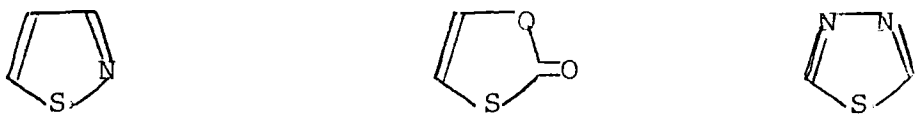
on photolysis.[86] Subsequently thiirenes (133) have been identified at low temperature by two groups independently.[87,88] It is noteworthy that carboethoxymethyl thiirene is stable up to 73K.[88] Other precursors (134)~(136) proved to be more



(132) (133)

R_1	H	CF_3	CH_3	CO_2Et
R_2	H	H	CO_2Et	CH_3

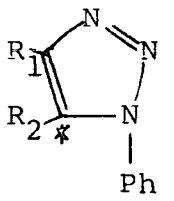
stable than (132) or gave other derivatives.[87] Their IR spectra are also in reasonable agreement with the theoretically calculated spectrum.[85]



(134) (135) (136)

(C) 2-Azirine

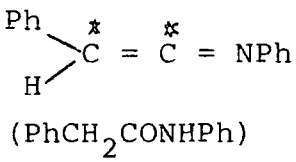
Loss of molecular nitrogen occurred from 1-H-1,2,3-triazole (137) photochemically and thermally.[89] Cyclic intermediates were suggested, as well as carbene and diradicals, because of a considerable degree of scrambling of the ^{13}C label in the product.[90] Other precursors (139) led to extrusion of nitriles, which may be due to homolysis of N-N bond.[91]



(137)

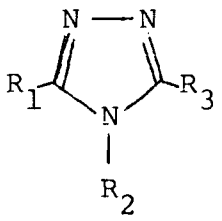
(a) R_1=H, R_2=Ph

(b) R_1=Ph, R_2=H



(PhCH$_2$CONHPh)

(138)



(139)

(a) R_1=R_3-H, R_2=Ph

(b) R_1=Ph, R_2=R_3=H

CHAPTER THREE

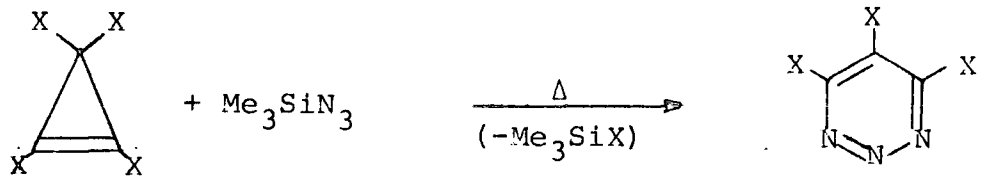
CHEMISTRY OF HALOGENATED-1,2,3- and -1,2,4-TRIAZINES

3.1 Introduction

Unlike halogenated-1,3,5-triazines, which have been known for some time, the chemistry of halogenated-1,2,3- and -1,2,4-triazines has been developed more recently, because these derivatives are much more difficult to synthesize.

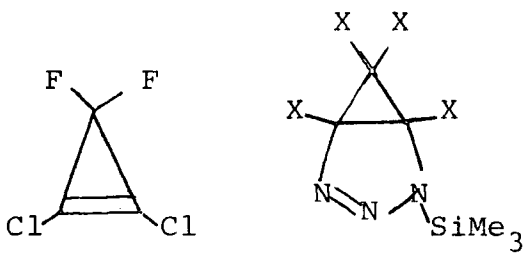
3.2 Halogenated-1,2,3-Triazines

Trichloro- and tribromo-1,2,3-triazines have been studied recently,[94] whereas fluorinated derivatives were unknown when this work began. The only synthetic routes are reaction of tetrahalogenocyclopropenes with trimethylsilylazide, to give the corresponding triazines in moderate yields. However, 3,3-



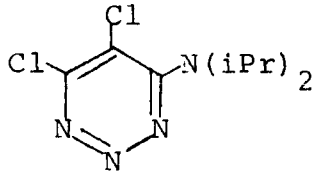
(X = Cl, Br)

difluoro-1,2-dichlorocyclopropene (140) does not react with the azide. Three intermediates are postulated (141)∿(143) in the process.

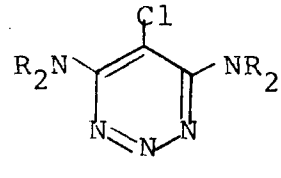


(140) (141) (142) (143)

These triazines are unstable with respect to hydrolysis, and not surprisingly, the other reactions reported are essentially nucleophilic aromatic substitutions. The order of reactivity of the positions to attack by nucleophiles is 4(6)- > 5- positions. However, the isolated product depends on the bulkiness of the nucleophiles, *i.e.*, di-isopropylamine gives mono-substitution (144), while dimethyl- and pyrrolidino-amines as well as methoxide and phenoxide give di-substitution (145a), (145b), (146a) and (146b) respectively.

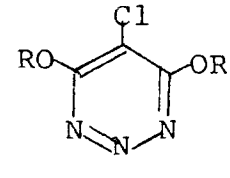


(144)



(145)

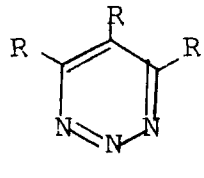
(a) R = Me
(b) R_2 = $(CH_2)_4$



(146)

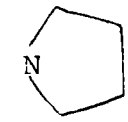
(a) R = Me
(b) R = Ph

Excess amounts of nucleophiles lead to tri-substitutions (147).

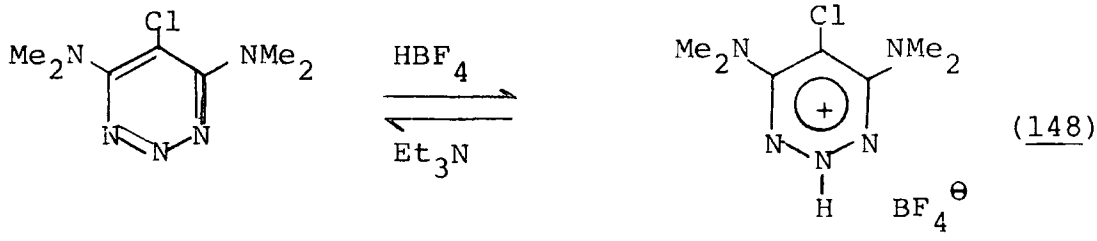


(147)

R = OMe, SEt, NMe_2, NEt_2,

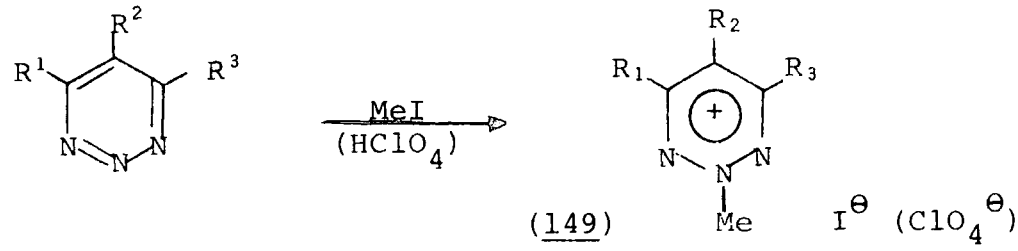
$N(iPr)_2$, 

Protonation of 1,2,3-triazines takes place primarily at N-2, but only the tetrafluoroborate salt (148) has been isolated.

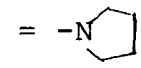


(148)

Likewise alkylation takes place at N-2 using methyliodide.



(149)

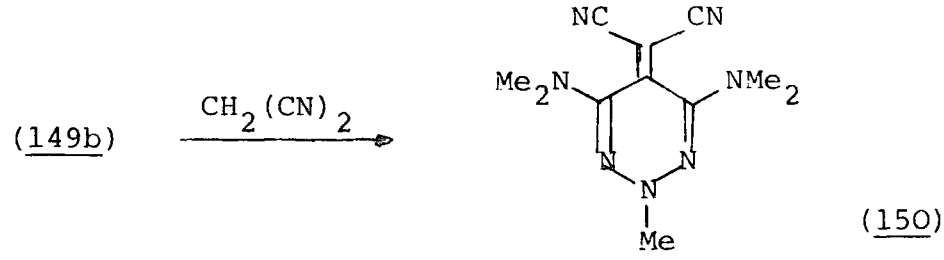
(a) $R^1 = R^2 = R^3 =$  , NMe_2, $N(iPr)_2$

(b) $R^1 = R^3 = NMe$, $R^2 = Cl$

(c) $R^1 = R^2 = N(iPr)_2$, $R^3 = H$

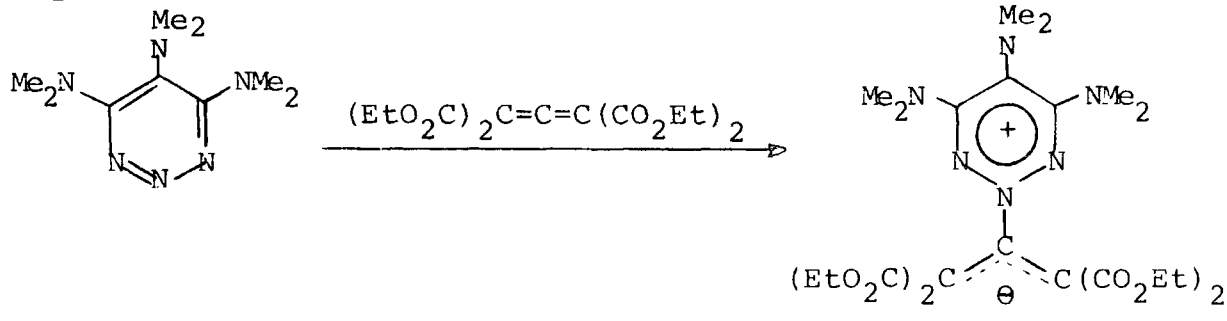
(d) $R^1 = R^3 = NEt_2$, $R^2 = N(iPr)_2$

Derivative (149b) reacts with malononitrile to form (150).

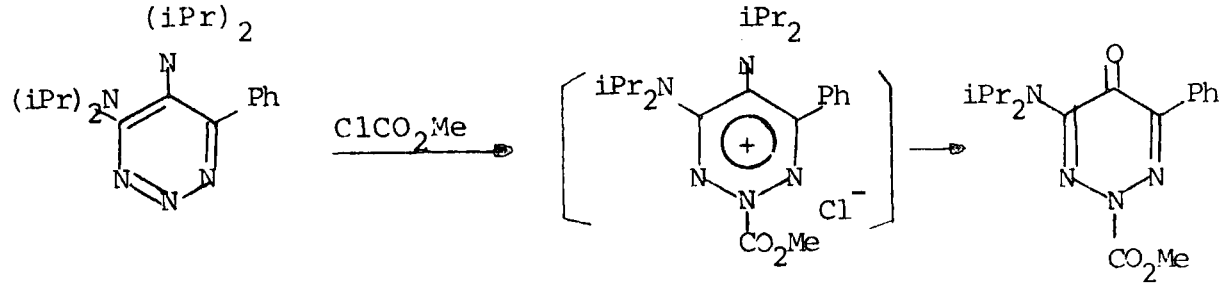


(150)

Acylation, arylation and reactions of allene and α-chloro enamine with amino-1,2,3-triazines also occurred at N-2. Attempted cycloaddition reactions failed.



(151)

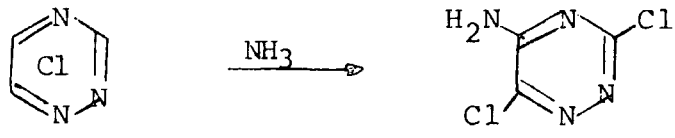


3.3 Halogenated-1,2,4-Triazines

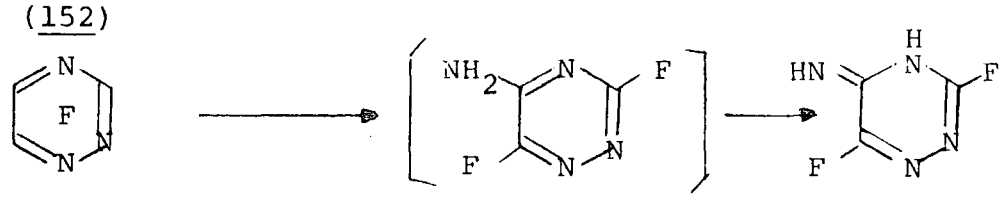
Trichloro-1,2,4-triazine (152) is prepared from 3,5-dihydroxy-1,2,4-triazines by using chlorinating reagents.[95] Vapour phase fluorination of (152) over potassium fluoride yields trifluoro-1,2,4-triazine (153). Polyfluoroalkyl derivatives are mainly obtained from (152) and (153).

(A) Trichloro- and trifluoro-1,2,4-triazine

Both derivatives, especially (153), are moisture sensitive, and nucleophilic substitution occurs easily at the 5-position.[96,97,98] The position of further substitutions depend on the conditions.

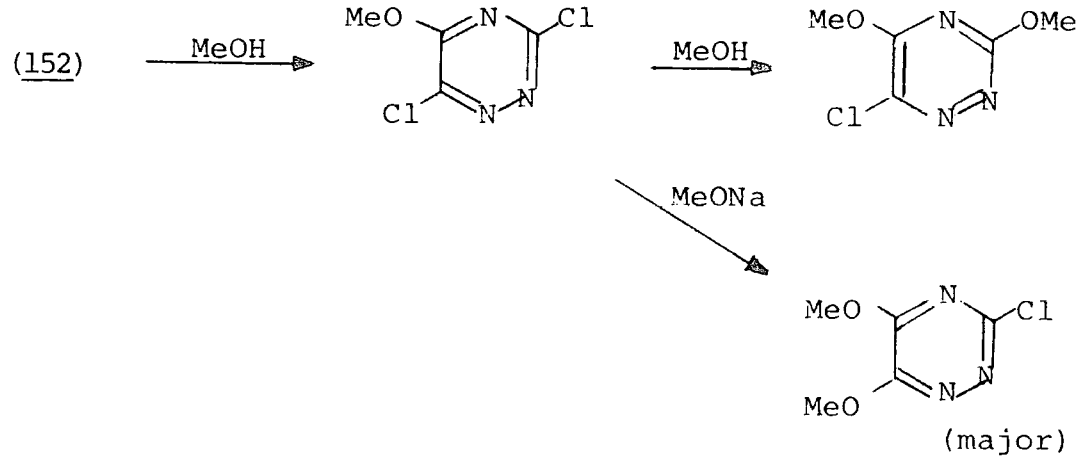


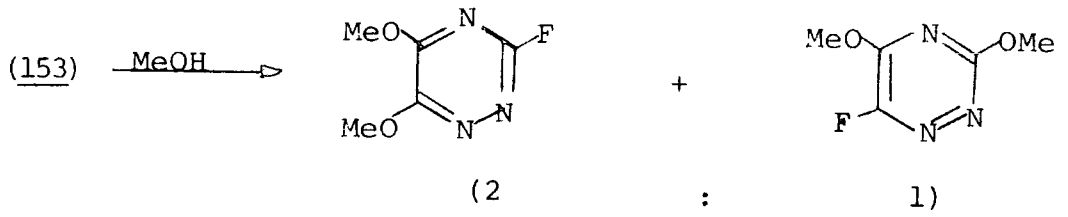
(152)



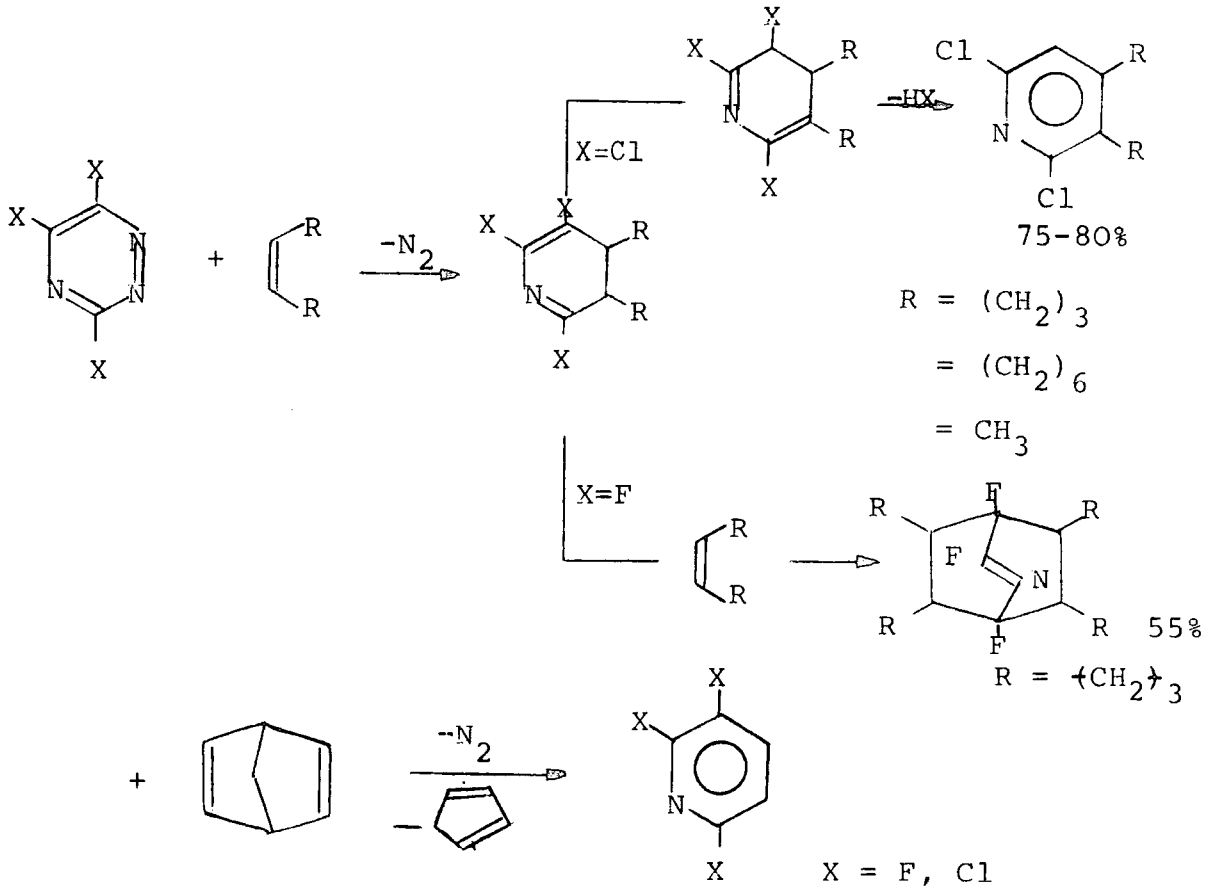
(153)

The positional order of reactivity is 5>3>6, using neutral nucleophiles such as dialkyl amines in both cases.[97,98] However,methanol reacts with (153) to form 5,6- and 3,5-di-substituted derivatives in 2:1 ratio,[95] whereas (152) gives only the expected 3,5-derivative. With sodium methoxide, (152) yields 5,6-derivative as a major product.[95]



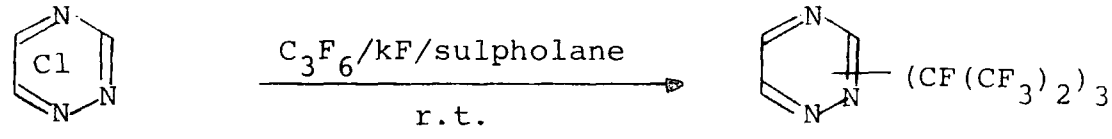


Both derivatives undergo [4+2] cycloaddition reactions with cis-olefins[99] like parent triazines.[8]



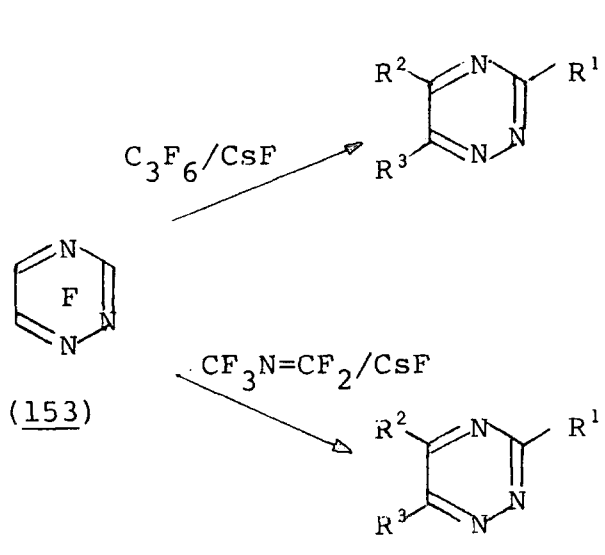
(B) Polyfluoroalkyl-1,2,4-triazines

Perfluoro-trisisopropyl-1,2,4-triazine (154) was obtained directly from (152) with hexafluoropropene using potassium fluoride.[11]



(152) (154)

Perfluoro-5-mono- and -3,5-di-isopropyl derivatives were prepared, along with (154) from (153).[24] Likewise perfluoro-dimethylamino derivatives were synthesized from (153) using perfluoro-2-azapropene and cesium fluoride without solvent.[24]



(153)

(a) $R^1=R^2=R^3=C_3F_7$

(b) $R^1=R^3=F$, $R^2=C_3F_7$

(c) $R^1=R^2=C_3F_7$, $R^3=F$

(d) $R^1=R^3=C_3F_7$, $R^2=F$ (minor)

(a) $R^1=R^3=N(CF_3)_2$, $R^2=F$

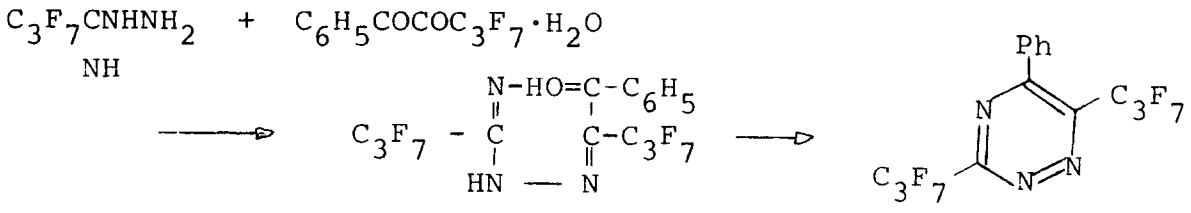
(b) $R^1=R^2=R^3=N(CF_3)_2$

(c) $R^1=R^3=F$, $R^2=N(CF_3)_2$

(d) $R^1=R^2=F$, $R^3=N(CF_3)_2$

[(c), (d) : minor]

3,6-Bis-heptafluoropropyl-5-phenyl-1,2,4-triazine was obtained in a different synthetic route.[100] Pyrolysis and photolysis (see Chapter Two) were well investigated, whereas other reactions have not been reported.



DISCUSSION

GENERAL INTRODUCTION

The aim of this project is principally to investigate a rational method to generate azetes and the background to this approach is contained in the chemistry described in Chapter Two.

The generation and trapping of unfused azetes remains a challenge and the main obstacle is the fragmentation of azetes to acetylenes and nitriles. Calculations suggest that the most promising derivatives could be fluoroazetes.[35] Perfluoroalkyl substitution could also stabilize the system, as seen in other 4π systems, if appropriate percursors are adopted. Hence the perfluoroalkyl group stabilizes many other small ring systems.[101]

The 1,2,3-triazine could be a better system than the 1,2,4-triazine and the oxazinone, since nitrogen elimination occurs under relatively mild conditions, which may suppress the further fragmentation. Thus fluorinated-1,2,3-triazines were the target compounds of this project.

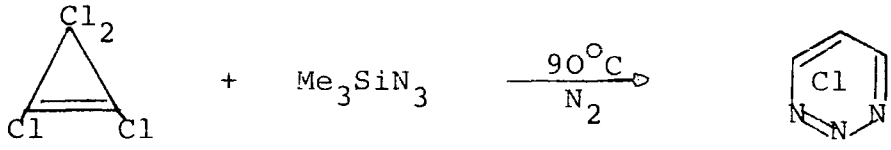
R_f = F, $-CF(CF_3)_2$

CHAPTER FOUR

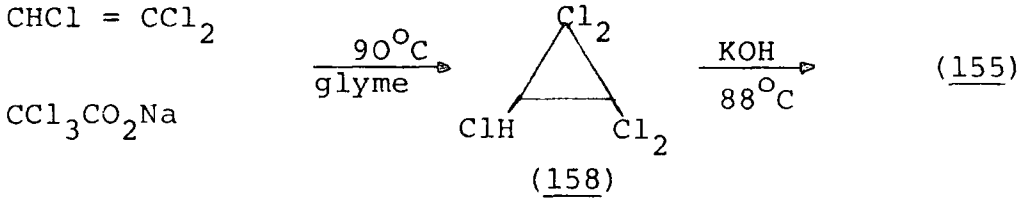
SYNTHESIS OF CHLORO- AND FLUORO-1,2,3-TRIAZINE DERIVATIVES

4.1 Trichloro-1,2,3-Triazine

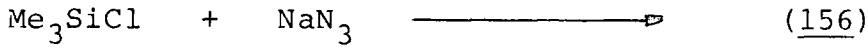
The synthesis of trichloro-1,2,3-triazine (157) has been reported recently by the reaction of tetrachlorocyclopropene (155) with trimethylsilyl azide (156) in 40% yield.[94] Both starting materials (155)[102,103] and (156)[104] were prepared as shown below.



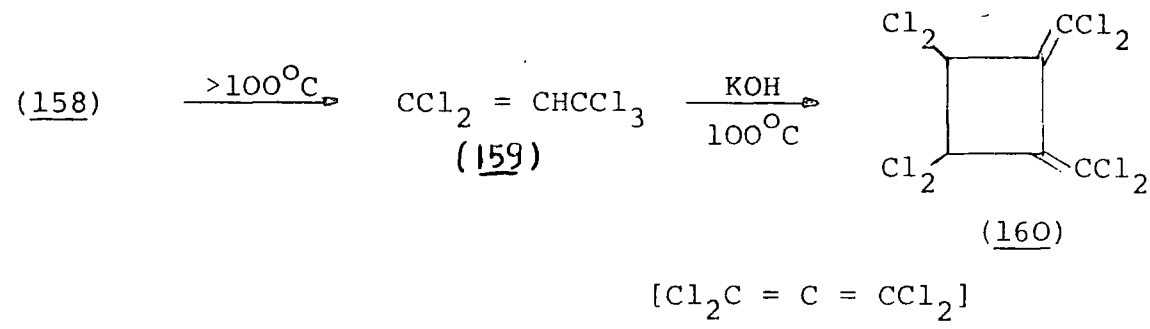
(155) (156) (157)



(158)



These procedures were adopted here but some observations may be usually recorded. Dehydrochlorination of pentachlorocyclopropane (158) is an extremely exothermic reaction; it starts around 80°C and becomes out of control above 100°C. Occasional cooling is essential and it is better to stop stirring above 90°C. Thermal isomerization of (158) to 1,1,3,3,3-pentachloropropene (159) takes place easily above 100°C.[102] The product (159) forms perchlorodimethylene cyclobutane (160) in the presence of alkali,[105] presumably *via* an allene intermediate.



(158) $\xrightarrow{>100^{\circ}C}$ $CCl_2 = CHCCl_3$ (159) $\xrightarrow[100^{\circ}C]{KOH}$ (160)

$[Cl_2C = C = CCl_2]$

Furthermore attention should be drawn to the formation of a gaseous by-product which irritates eyes severely; the structure of the by-product is unknown.[103] A second point concerns the purification of (157); the triazine (157) is formed together with a large amount of a brown powder which is not stable on heating, since attempted sublimation of the crude mixture led to explosion. It is probable that the powder may contain azide derivatives (141)∿(143),[94] although no further investigation was made. It was found that Soxlet-extraction or hot filtration with diethyl ether, followed by sublimation provided colourless crystals of (157) safely.

4.2 Trifluoro-1,2,3-Triazine

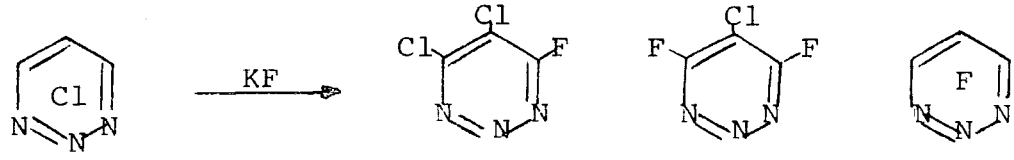
(A) Introduction

One of the most useful routes to highly fluorinated heteroaromatics involves the use of potassium or other alkali metal fluorides in nucleophilic displacement of chlorine by fluorine, from activated aromatic systems.[106] However, a determination of the most effective conditions for a particular system is clearly a matter of importance. Pentachloropyridine is converted to pentafluoro-derivative with potassium fluoride in the absence of a solvent.[107] The very reactive trichloro-1,3,5-triazine only requires sodium fluoride in the liquid phase,[108]

whereas trichloro-1,2,4-triazine needs short contact with potassium fluoride in the vapour phase[98] for the successful fluorination.

(B) Fluorination of trichloro-1,2,3-triazine

Reaction of (157) with potassium fluoride was carried out by various methods. 4,5-Dichloro-6-fluoro- and 5-chloro-4,6-difluoro-1,2,3-triazines [(161) and (162) respectively] were obtained, together with a trace amount of trifluoro-



(157) (161) (162) (163)

derivative (163) in a Carius tube reaction at 180°C in *ca.* 60~65% yield. A mixture of (161) and (162) was also formed in an aprotic solvent (35%). However, neither method afforded (163) as a major product and sometimes led to red-brown tar, suggesting that the triazine (163) is highly reactive.

Vapour phase fluorination, a process suitable for very reactive systems, was applied to afford mainly (161) and (162) in high yield (*ca.* 90%) at a temperature below 500°C, and (163) in moderate yield (*ca.* 50%) above 600°C. The low thermal stability accounts for the limited yield of (163). Therefore a two-stage fluorination procedure was adopted, where the temperature of the furnace was 500°C and 600°C, respectively. The chlorofluoro-derivatives obtained from first stage were sufficiently stable enough to react at 600°C. This gave (163) in 70% yield, together with (162) (15%).

The triazine (163) is a lachrymatory clear liquid and very moisture sensitive, forming a dark red oil with time, as was observed in the case of trifluoro-1,2,4-triazine.[98] The ^{19}F n.m.r. spectrum of (163) shows two absorptions with F-F coupling constant 22Hz, which are analogous to those found in fluorines at the 4-, 5- and 6-positions on perfluoro pyrimidine ring.[109]

4.3 Perfluoroisopropyl-1,2,3-Triazines

(A) Introduction

A range of perfluoroalkyl derivatives of highly fluorinated aromatics has been obtained in fluoride-ion induced reactions of activated haloaromatic compounds with fluorinated alkenes.[106,110] These are reminiscent of the Friedel-Crafts reactions in hydrocarbon chemistry.

$$F^{\ominus} + F_2C=C< \rightleftharpoons CF_3-\overset{\ominus}{C}< \xrightarrow{ArX} CF_3-\overset{|}{\underset{|}{C}}-Ar + X^{\ominus}$$

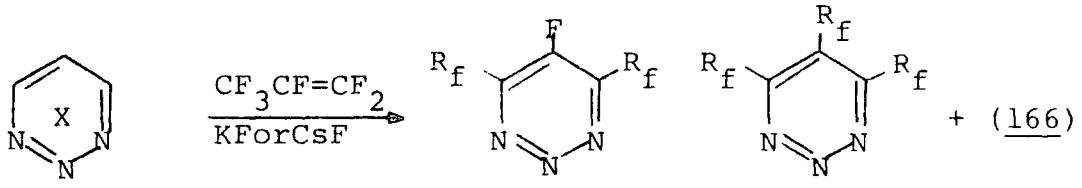
$$H^{\oplus} + H_2C=C< \rightleftharpoons CH_3-\overset{\oplus}{C}< \xrightarrow{ArH} CH_3-\overset{|}{\underset{|}{C}}-Ar + H^{\oplus}$$

Generally this method employs polyfluoroaromatics as starting materials but, in certain cases,[11,111] has been extended to chloroaromatics. One of them has been developed in this laboratory to obtain perfluorotrisisopropyl-1,2,4-triazine from the trichloro-derivative with hexafluoropropene.[11]

(B) Polyfluoroalkylation of halogeno-1,2,3-triazines

Polyfluoroalkylation of trichloro- and trifluoro-1,2,3-triazines was attempted with hexafluoropropene in the presence

of potassium- or cesium-fluoride in aprotic solvents. In all cases, perfluoro-4,6-bisisopropyl- and-4,5,6-trisisopropyl-1,2,3-triazines were obtained, together with a very unusual product [(164), (165) and (166) respectively], besides hexafluoropropene oligomers. The composition of the product



X = F, Cl (163) (157)

(164) (165)

+ $\{C_3F_6\}_n$ n = 2,3

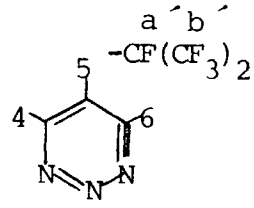
(Rf = $CF(CF_3)_2$)

varied principally with the reaction temperature. Derivative (164) becomes a predominant product below 20°C, while higher temperature favours formation of (165), indicating that the adjacent perfluoroisopropyl groups protect the 5-position from attacking of perfluoroisopropyl anion. Analogous observation was made for polyfluoroalkylation of perfluoropyrimidine.[113] However, above 40°C, the compound (166) becomes the major component. The total yield at 20°C was 48.4% [(164), (165), and (166) in 24.7, 19.2 and 4.5% respectively] under optimum conditions.

Structures of white crystal (164) and the yellow oil (165) were determined on the basis of their ^{19}F n.m.r. spectra, which also illustrates restricted rotation as represented by fixed conformations, (164a) and (165a) and these are analogous to those by perfluoroisopropyl groups in pyridine,[112] pyrimidine,[113]

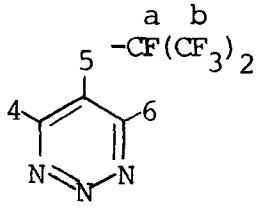
TABLE 4.1 N.M.R. Spectra of (165)

^{19}F n.m.r. spectrum (neat; ext. ref. $CFCl_3$)



Shift (ppm)	Structure	Intensity	Assignment
172.4	D(J=39Hz)	6	5b´
174.5	D(J=17.5Hz) of D(J=3.9Hz)	6	4b´
175.3	S	6	6b´
154.7	D(J=117Hz) of Sept (J=4.0Hz)	1	5a´
180.3	D(J=117Hz) of Sept (J=3.9Hz)	1	4a´
184.6	Sept (J=39Hz)	1	6a´

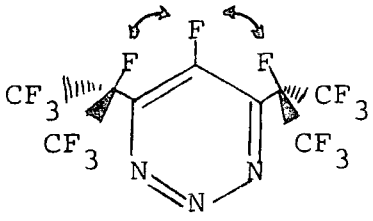
^{13}C n.m.r. spectrum [$(CD_3)_2C=O$; int. ref. TMS]



Shift (ppm)		Structure	Intensity	Assignment
148.1	(145)[a]	D(J=27.9Hz)	1	6
145.5	(145)[a]	D(J=29.3Hz) of D(J=2.8Hz)	1	4
119.0		Q(J=288.3Hz) of D(J=27.8Hz)	4	4b,6b
118.9		Q(J=289.2Hz) of D(J=26.5Hz)	2	5b
118.0	(116)[a]	D(J=30.3Hz)	1	5
93.8		D(J=175.4Hz) of Sept(J=365.Hz)	1	5a
92.8		D(J=217.0Hz) of Sept(J=34.0Hz)	2	4a,6a

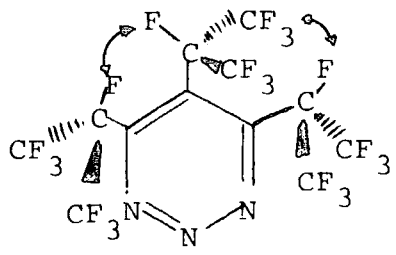
(a) Calculated values

J = 45.4Hz



(164a)

J=117Hz 39Hz



(165a)

and pyrazine[114] systems. The fixed conformation of (165) also affects the ^{13}C n.m.r. spectrum, where the chemical shifts of carbons at the 4- and 6-positions are slightly different (Table 4.1) and are close to calculated values by taking into account the substituents effects.[115]

Both triazines (164) and (165) show clear peaks corresponding to loss of nitrogen besides the parent peak in their mass spectra .

The structure of (166) is discussed in the following chapter.

CHAPTER FIVE

AN UNUSUAL POLYFLUOROALKYLATION PRODUCT

5.1 Structure

The molecular weight of the unusual product, a yellow viscous oil (166), is 735, *i.e.* 150 higher than perfluorotrisisopropyl-1,2,3-triazine (165), suggesting the reaction of four equivalents of hexafluoropropene in the formation of (166) from halogeno-1,2,3-triazines.

In fact the ^{19}F n.m.r. spectrum of (166) (Table 5.1) shows four pairs of non-equivalent trifluoromethyl groups and three tertiary fluorines, two of which are equivalent. This spectrum immediately rules out participation of hexafluoropropene oligomers, which could lead to a product containing fluorine atoms at vinylic sites. A remarkable feature of (166) is that two pairs of trifluoromethyl groups become identical above 75°C as demonstrated by the ^{19}F n.m.r. spectrum. Clearly, therefore, the compound (166) has a symmetric structure. ^{13}C n.m.r. also reveals the symmetry of the system, where two equivalent perfluoroisopropyl groups and unsaturated carbons are observed. Furthermore ^{15}N n.m.r. shows two identical nitrogens out of three. These data indicate that the product (166) is one of the possible symmetric structures as shown below. However, the ^{13}C n.m.r. and UV spectra eliminate the possibility of (166a) by the comparison with those of (165). Furthermore, the fact that CF_3-F coupling (J=39.5Hz) remains unchanged at 100°C suggests that the structure is (166b), hence the restricted rotation is more readily explained. The chemical

TABLE 5.1 N.M.R. Spectra of the Compound (166)

^{19}F n.m.r. spectra (neat, ext.ref. $CFCl_3$)

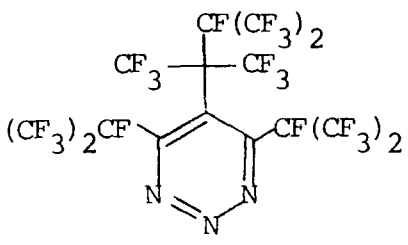
Room Temperature			100°C		
Shift (ppm)	Structure	Intensity	Shift (ppm)	Structure	Intensity
61.3	D(J=39.5Hz)	6	61.4	D(J=39.5Hz)	6
72.9	S	6	75.4	S	12
77.7	S	6	77.9	S	6
78.2	S	6			
153.4	S	1	153.0	S	1
177.6	Q(J=39.5Hz)	2	176.7	Q(J=39.5Hz)	2

^{13}C n.m.r. spectrum (solvent $(CD_3)C=O$; int.ref.TMS)

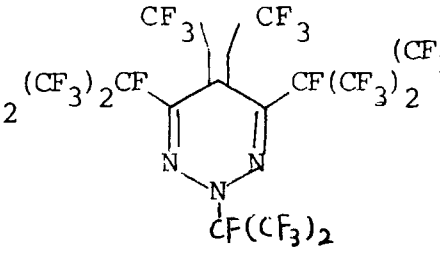
Shift (ppm)	Structure	Intensity
125.5	D(J=36.9Hz)	2
122.3	Sept (J=34.2)	1
118.9	Q(J=288.4) of D(J=26.1)	4
118.86	Q(J=279.2)	2
118.2	Q(J=289.3) of D(J=29.4)	2
117.8	S	1
97.2	D(J=236.2) of Sept (J=35.9)	1
92.9	D(J=216.6) of Sept (J=35.4)	2

^{15}N n.m.r. spectrum (solvent $CF_2ClCFCl_2/(CD_3)_2C=O$; ext.ref.$MeNO_2$)

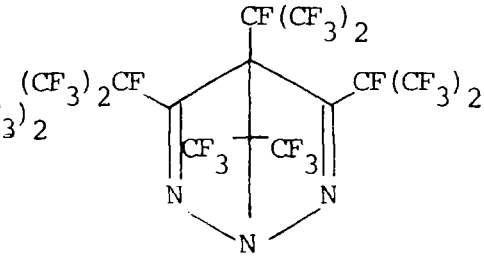
Shift (ppm)	Structure	Intensity
-46.4	S	2
+40.2	D(J=14Hz)	1



(166a)



(166b)



(166c)

shift (61.3 p.p.m) also supports the presence of a perfluoro-isopropylidene group,[116,117,118] although the value seems to be consistent with bridgehead trifluoromethyl groups[119,120,121] which is different from those in perfluoroisopropyl groups.[122]

Ultraviolet spectra

Compound	λ max (nm)	ε (ℓ mole^{-1} cm^{-1})
(166)	288	7300
(165)	231	2327
	300, 346	(shoulder)

In order to confirm the structure, reaction of (166) with diazomethane was carried out, forming a 1:1 adduct (167) in good yield (85%). The ^{13}C n.m.r. spectrum of (167) (Table 5.2) clearly shows that the symmetry of the system as well as two unsaturated carbons were preserved, while the chemical shifts of two carbons were shifted to upper field significantly after the reaction. Moreover, in the ^{19}F n.m.r. spectrum, CF_3-F coupling disappeared, synchronized with up-field shift. These results indicate that (166) could have three sites of unsaturation, confirming that the structure is (166b), which is also supported by its i.r. spectrum where two absorptions at 1610 and 1535 were observed. The structure of (167) as Δ^2 pyrazoline is established by considering its ^1H n.m.r. and i.r. spectra.[123]

TABLE 5.2 N.M.R. Spectra of (167)

^{19}F n.m.r. spectrum ($CDCl_3$; int.ref. $CFCl_3$)

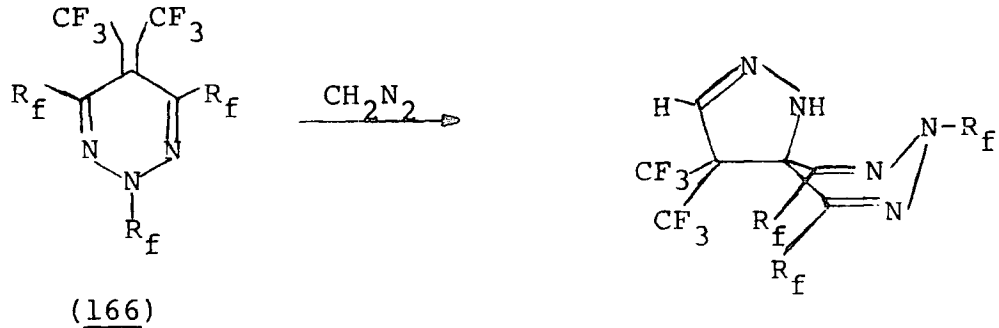
Shift (ppm)	Structure	Intensity
65.7	D(J=11.3Hz)	6
72.7	T(J=4.7Hz)	6
75.5	T(J=4.7Hz)	6
77.1	S	6
153.4	S	1
184.3	S broad	2

^{13}C n.m.r. spectrum ($(CD_3)_2C=O$; int.ref. TMS)

Shift (ppm)	Structure	Intensity
126.1	S	(1)
125.8	D(J=30 Hz)	2
120.3	Q(J=284.7 Hz)	2
119.1	Q(J=289.1) of D(J=25.9)	2
118.9	Q(J=288.2) of D(J-29.1)	2
118.1	Q(J=289.6) of D(J=29.7)	2
96.2	D(J=235.1) of Sept(J=35.5)	1
92.9	D(J=223.2) of Sept(J=33.1)	2
76.2	Sept (J=27.7)	1
63.3	S	1

^{1}H n.m.r. spectrum ($(CD_3)_2C=O$; int.ref. TMS)

Shift (ppm)	Structure	Intensity
7.2	S	1
8.4	S broad	1



(166)

(167)

$(R_f = CF(CF_3)_2)$

Reactions of diazomethane with perfluoroalkyl-alkenes[123] and -imines[124,125,126] have been reported. In both cases reactions take place with ease. However the imine function does not participate in the reaction in this particular case, suggesting that these functional groups are sterically protected by perfluoroisopropyl groups.

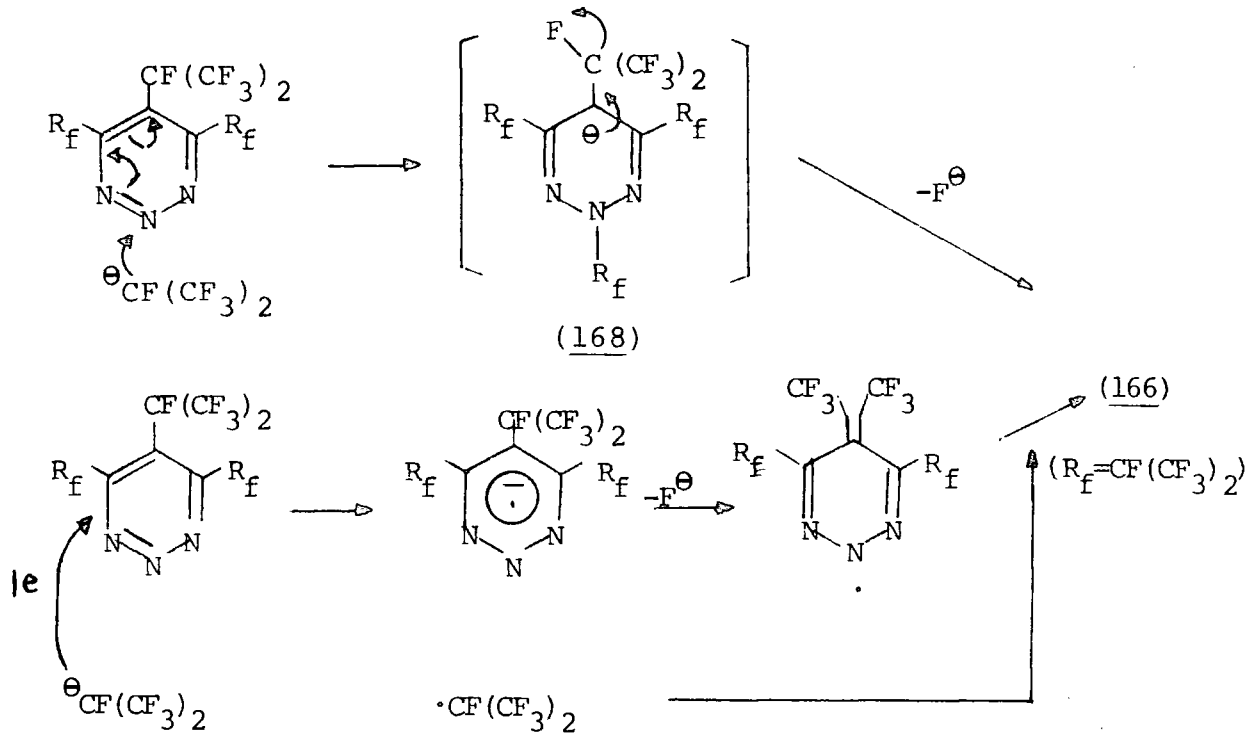
Cycloaddition reactions with 2,3-dimethyl butadiene, tetramethylethylene, phenylazide, and dimethylacetylenedicarboxylate were attempted without success, which shows that the reactivity of perfluoroisopropylidene group is analogous to perfluoroalkyl alkenes,[123] though it is conjugated with the imine functions.

5.2 Mechanism

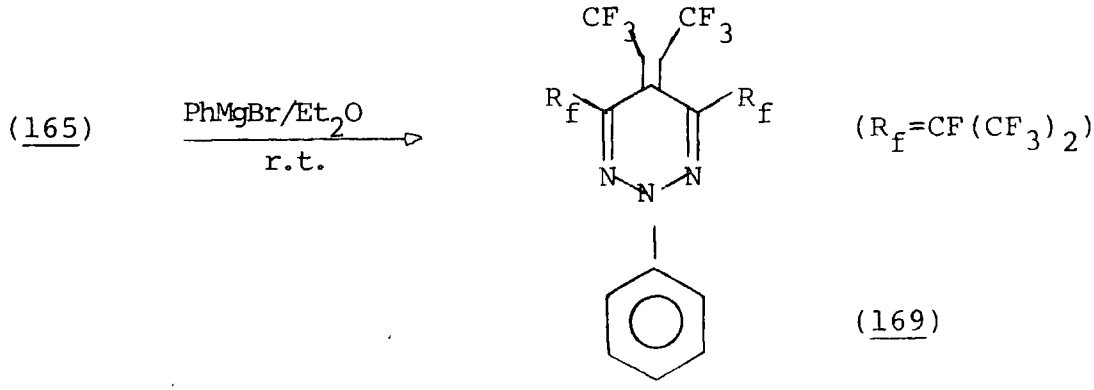
Two mechanisms could be proposed for the formation of (166) since the product (166) was obtained quantitatively from (165). They are a nucleophilic reaction process and one electron transfer process[127] as shown in Scheme 5.1. In order to distinguish between the two processes, reaction of (165) with phenyl magnesium bromide was attempted, to give phenyl substituted derivative (169) as a slightly brown viscous liquid,

with the characteristic fluorine chemical shift (60.3 ppm) in the perfluoroisopropylidene group and CF_3-F coupling (J=37Hz). More important, formation of biphenyl was not detected, making clear contrast to the radical process[128] ascribed earlier. Furthermore the product (166) was obtained

Scheme 5.1



even in the presence of oxygen. These results argue against the one electron transfer process,[127] and indicate that the

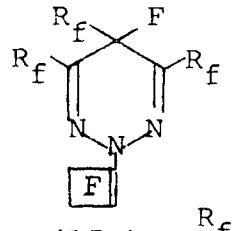
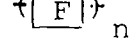
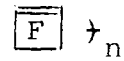


process involves nucleophilic attack on the central nitrogen, followed by elimination of fluoride ion on the perfluoroisopropyl group at the para position. The mechanism could be the first example of nucleophilic attack on nitrogen in a heterocyclic compound and is in good contrast to those of 1,2,3-triazines with electron-donating groups,[94] where protonation and alkylation occur at the nitrogen (see Chapter Three). It is clear that the presence of the perfluoroisopropyl groups has left the central nitrogen atom extremely electron deficient and therefore, surprisingly susceptible to nucleophilic attack, (for further confirmation of the mechanism and reactions, see Chapter Eight).

5.3 Derivatives of Other Fluorinated Alkenes

In order to develop the reaction process, attempts were made to obtain other fluorocarbon derivatives. These results are summarized in Table 5.3, which may be rationalized from a mechanistic point of view as shown in Scheme 5.2. The triazine (165) exists in equilibrium with nitranion form (171) in the presence of fluoride ion at the reaction temperature. The intermediate (171) reacts readily with perfluorocyclobutene, followed by loss of fluoride ion to yield the product (170) whose structure is determined by the spectroscopic data and comparison with cyclobutene derivatives.[129] Perfluorocyclobutene has been reported as an effective trapping agent of fluorinated nitranions.[129,130] However, without such reagents, the anion (171) loses perfluoroisopropyl group to form (164) since polyfluoroalkylation is a reversible process.[110] In fact, the

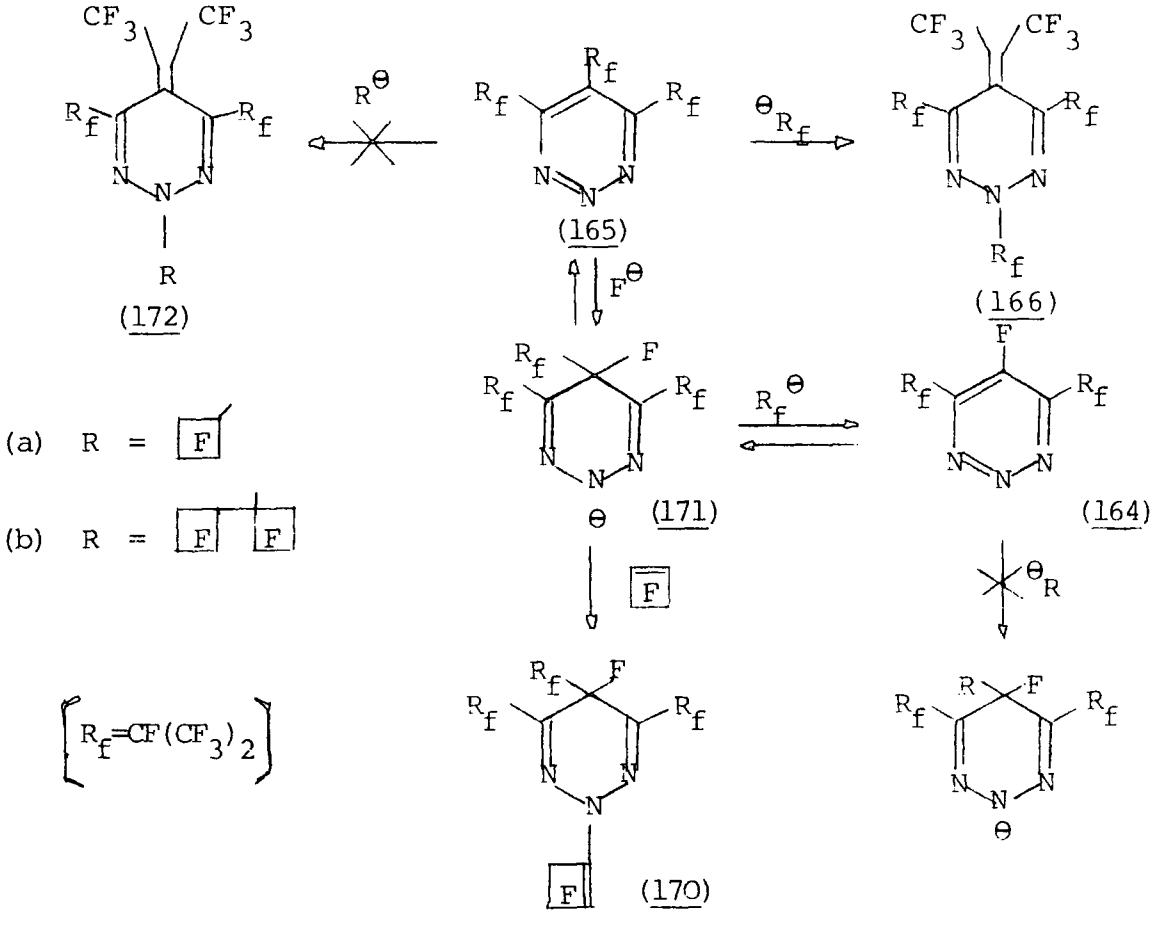
TABLE 5.3 Fluoride-ion Induced Reaction of (165) with Fluorinated Alkenes

Fluorinated Alkene	Product (yield)		
	 (170) R_f=$CF(CF_3)_2$		
 (98 / 2)	(170) (56.3%)	(166) (13.4%)	 n = 3
$(CF_3)_2C = O$		(166) (31%)	$+C_3F_6+_n$ n = 2.3
-	(164) (1.0%)	(166) (30.9%)	$+C_3F_6+_n$ n = 2.3
$CF_3C{\equiv}CCF_3$		Polymer	

Catalyst; CsF, Solvent; Tetraglyme, 60°C

triazine (164) was detected. The released perfluoroisopropyl anion reacts readily with (165) to afford (166) as expected. On the other hand perfluorocyclobutyl- and perfluoro+1-cyclobutyl+cyclobutyl-anions did not form any product such as (172). It is probable that the nucleophilicity of these anions is not high enough to attack the nitrogen at the 2-position. Hence perfluoro+1-cyclobutyl+cyclobutyl anion

Scheme 5.2



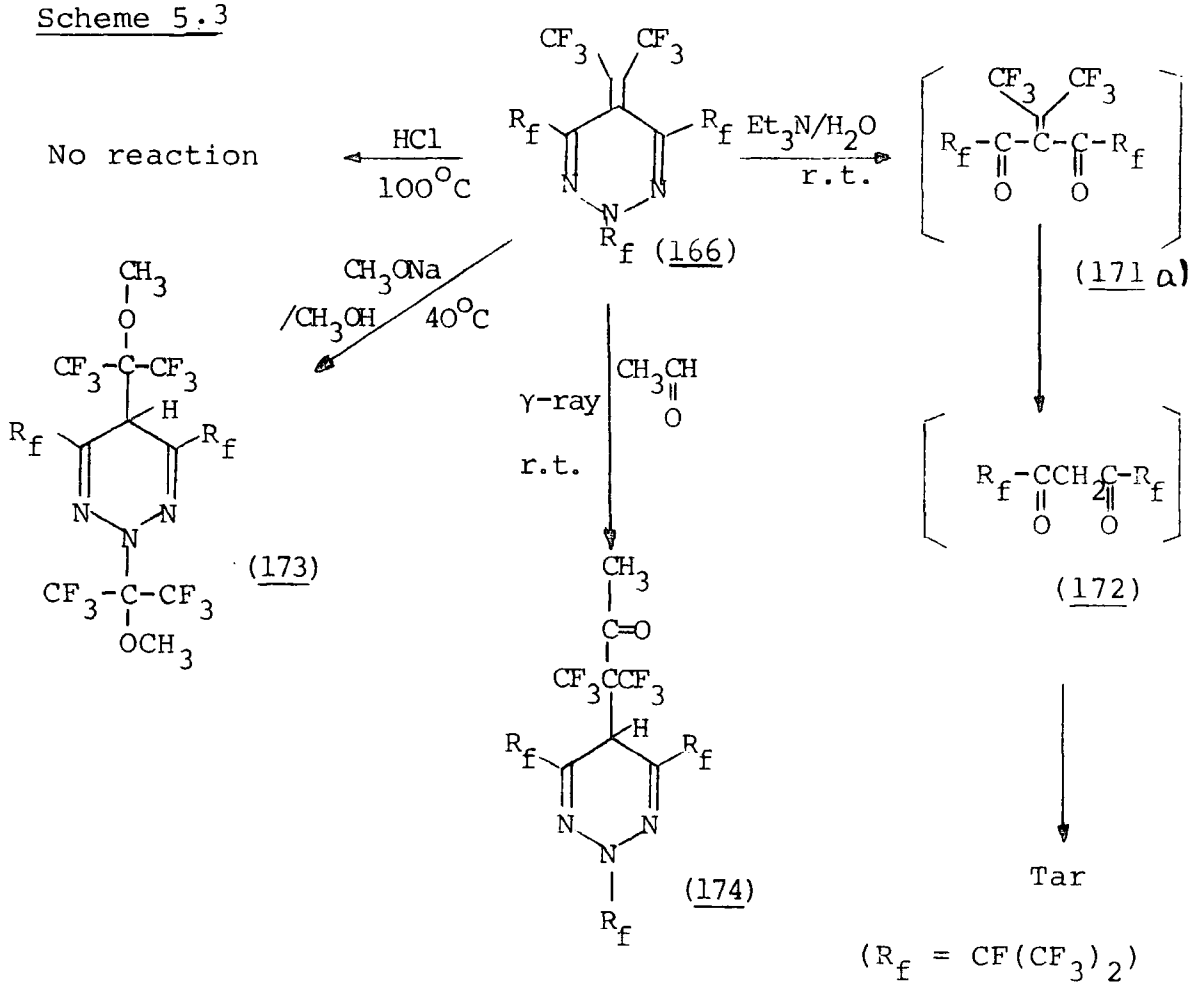
was observed under these conditions[131] and perfluorocyclobutene oligomers were obtained, which indicates formation of perfluorocyclobutyl anion. Furthermore, only perfluorotrisisopropyl-1,2,4-triazine was formed among the attempted reactions of trichloro-1,2,4-triazine with perfluoro-ethylene, -propene, -butene, and cyclobutene[132], which is also consistent with these observations.

In addition, perfluoroisopropyloxy anion may not be stable at the temperature since at low temperature the anion reacts with trichloro-1,3,5-triazine to give perfluoroisopropoxy-1,3,5-triazine.[133] Perfluorobut-2-enyl anion is reactive enough to undergo homopolymerization[134] and could be partly trapped by perfluoropyridazine[135] and fluoroalkenes,[134] but not in this case.

5.4 Reactions of the unusual Product

Various reactions were attempted with (166), which are summarized in Scheme 5.3. Compound (166) is quite stable against acid but under basic conditions, gave mainly high molecular weight tar. The intermediates (171a) and (172) are suspected from ^{19}F n.m.r.[136] and mass spectral data, which may undergo further condensation reaction to form tar. In contrast, the reaction of methoxide afforded a white solid (173) in 59% yield. Radical addition of acetoaldehyde to (166) yielded a 1:1 adduct (174) in 84% yield. (Both products (173) and (174) again confirm the strucutre (166b).) These reactions significantly reveal the chemical properties of (166). The sensitivity to base is typical of imine functions[137] but not to methoxide because bulky perfluoroalkyl

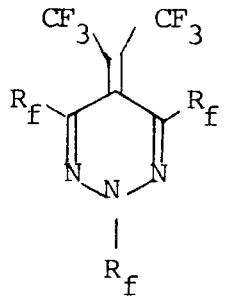
Scheme 5.3



substituents may act as protecting groups. In addition, the substituents protect the molecule against acid by the nature of electron-withdrawing groups. The reactivity towards radical addition is analogous to those found in fluorinated alkenes.[138,139]

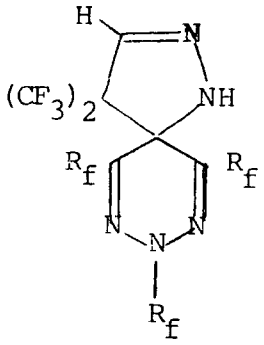
5.5 Physical Properties of the Derivatives

Five derivatives of (166) have been synthesized, *i.e.* (167), (169), (170), (173) and (174). Their appearance ranges from liquids to solids by the introduction of polar substituents. Since the compound (166) and the derivatives are conjugated systems, their electronic states may be most readily revealed by their UV spectra, as shown in Figure 5.1. λ_{max}, observed in (167), (170), (173) and (174) are consistent with those found for imine functions,[140,141] with much larger absorption coefficients than hydrocarbons. They are attributed to $n\rightarrow\pi^*$ transition, since polar solvents cause hypsochromic shifts and the absorptions disappear in acidic solution.[141] The observed hypsochromic shifts from that of (166) are apparently due to destruction of the conjugation. In contrast, that of (169) is significantly shifted bathochromically, indicating an extension of conjugation to the benzene ring through nitrogen. The extent of bathochromic shift is proportional to the magnitude of resonance effects of substituents in mono-substituted benzenes.[142] The observed λ_{max} (354nm, ε=12300; 247nm, ε=5600; 204nm, ε=14000) are close to those in benzophenone[143] (333nm, ε=165:$n\rightarrow\pi^*$; 254nm, ε=18000:p(^{1}La)) and nitrobenzene[144] (330nm, ε=165:$n\rightarrow\pi^*$; 280nm, ε=1000:α(^{1}Lb); 252nm, ε=9500) but considerably longer wavelength than dimethylaniline[145] (299nm, ε=2100:α(^{1}Lb))



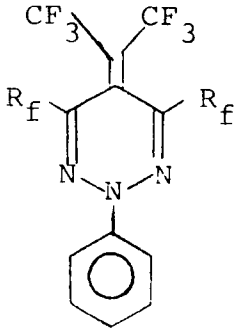
liq.bp.196°C

(166)



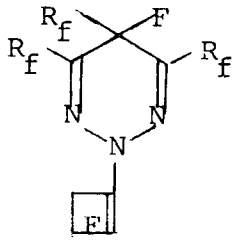
solid mp.62-68°C

(167)



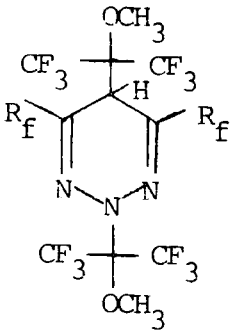
liquid

(169)



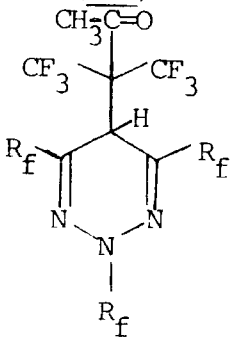
solid mp.46-47°C

(170)



solid mp.35-36°C

(173)



liquid

(174)

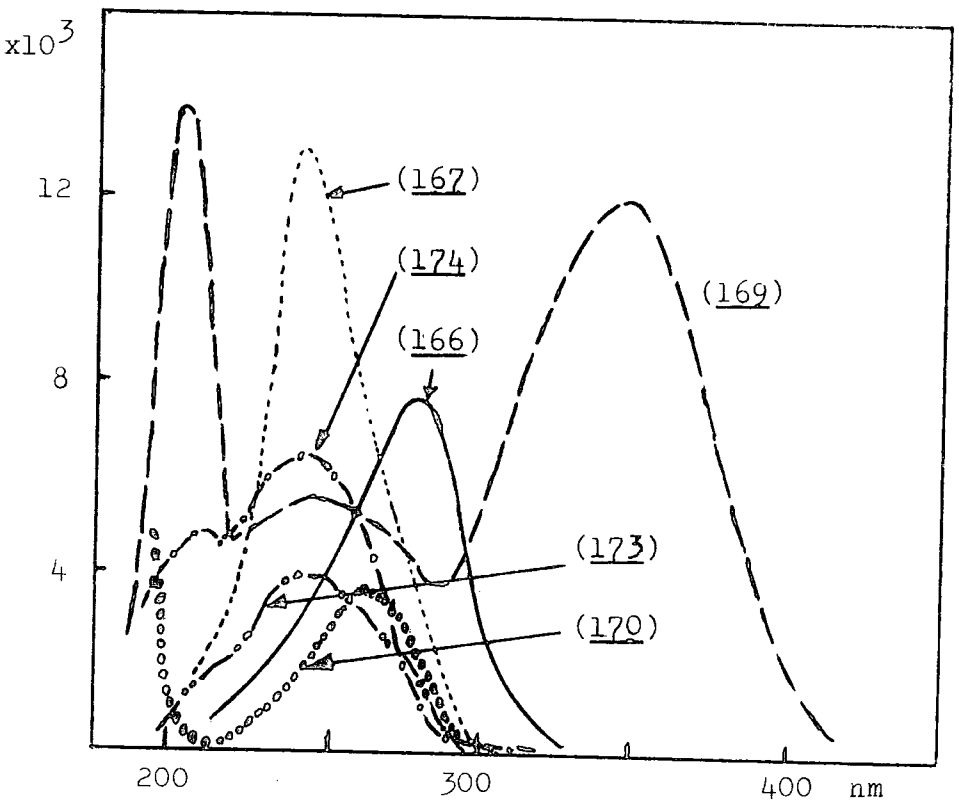


Figure 5.1 UV Spectra of the Derivatives

and styrene (282nm, ε=760, $\alpha(^1Lb)$).[145] Bridgehead nitrogens in organic semi-conductors are expected to have analogous effects.[146]

CHAPTER SIX

PYROLYSIS

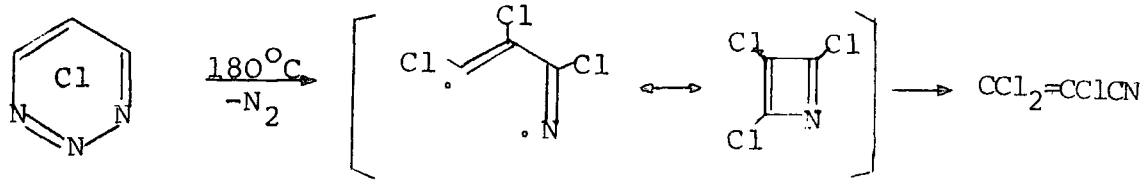
6.1 Introduction

Thermal elimination of nitrogen has been investigated extensively from 1,2,3- and 1,2,4-triazine systems to give acetylenes and nitriles in most cases as discussed in Chapter Two. In addition 1,2-diazine or pyridazines also extrude nitrogen on pyrolysis to yield acetylenes without nitriles[22,23] although the main process was rearrangement to pyrimidines and pyrazines.[147,148] Only two azetes, isolated so far, have been produced on flash pyrolysis.[9,10] Furthermore, possible formation of an azatetrahedrane is suggested by theoretical study.[34]

In this chapter attempts are discussed to generate azetes from halogenated-1,2,3-triazines on pyrolysis, as well as pyrolysis of the unusual product (166).

6.2 Trichloro-1,2,3-Triazine

Static pyrolysis of trichloro-1,2,3-triazine (157) at 180°C for 16 hrs. gave trichloroacrylonitrile (34) in 60% yield. The nitrile (34) is the same product obtained on pyrolysis of trichloro-1,2,4-triazine (32).[11] However, in

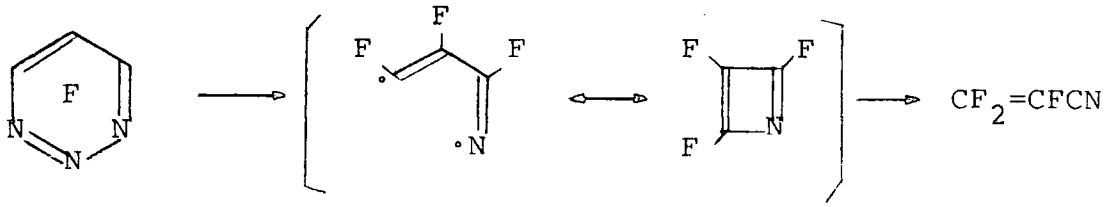


(157) (33c) (33b) (34)

this case, it is not certain whether (34) was formed directly from the diradical intermediate (33c) by migration of chlorine or *via* the cyclic species (33b). Trapping the intermediate with hexafluorobut-2-yne was attempted at 200°C to yield (34), though at 280°C a small amount of a 1:1 adduct was obtained (detected by mass spectrometry) among many liquid products and hexakistrifluoromethyl benzene,[149] as well as a large amount of polymeric product. Further investigation was not made.

6.3 Trifluoro-1,2,3-Triazine

Static pyrolysis of trifluoro-1,2,3-triazine (163) at 350°C for 4 hrs. gave only black tar but in the presence of naphthalene as a solvent, a liquid product was formed. The product consisted mainly of perfluoroacrylonitrile (176) as indicated by ^{19}F n.m.r.[150] and i.r.[151] spectra and mass spectrometry, although the yield was only 8%. The



(163) (175) (176)

nitrile (176) could not confirm the formation of trifluoroazete (175) as in the case of (34). An attempt to trap the intermediate with hexafluorobut-2-yne was made without success, giving black polymer. Flash pyrolysis of (163) above 700°C yielded a yellow coloured product on a cold finger. However, the product solidified during warming up to room temperature

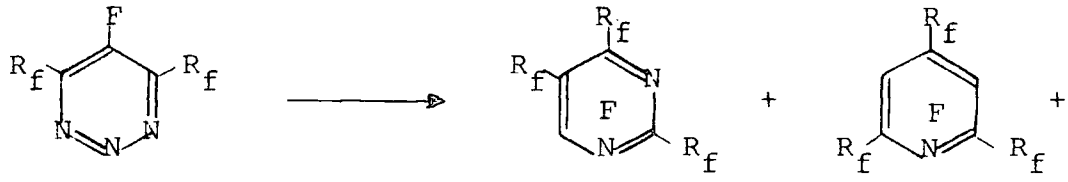
and contained nitrile groups, detected by i.r. spectrum. These results make good contrast to trifluoro-1,2,4-triazine (53),[99] and tetrafluoropyridazine,[147] where rearrangements to trifluoro-1,3,5-triazine (54) and tetrafluoropyrimidine were observed respectively.

6.4 Perfluoro-4,6-bisisopropyl-1,2,3-Triazine

(A) Static Pyrolysis

Pyrolysis of perfluoro-4,6-bisisopropyl-1,2,3-triazine (164) at 330°C for 2 hrs. yielded a wide range of products. Major components are perfluoro-2,4,5-trisisopropylpyrimidine (177), perfluoro-2,4,6-trisisopropylpyridine (178), perfluoroisobutyronitrile (46), and perfluoro-3-methylbut-1-yne (179). Also obtained were a dimer (180) of the corresponding azete (181) and a dimer of the acetylene (182) as minor products.

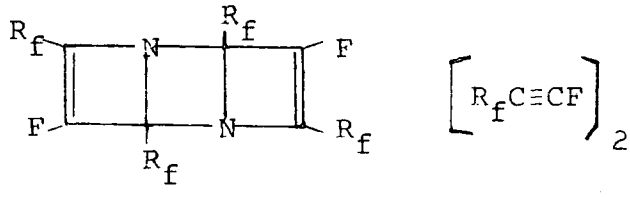
Structure of (177) follows from its spectroscopic properties, as shown in Table 6.1; the medium bands at 1500 and 1600 cm^{-1} in the i.r. spectrum are similar to these polyfluoroalkylpyrimidine (λ_{max} 1603 and 1545 cm^{-1}),[148] but distinct from pyrazines[148] (transparent). The u.v. spectrum indicates the pyrimidine systems (perfluoroalkyl-tetra- and -2,4,6-trisisopropylpyrimidines,[113] λ_{max}; 220 and 257nm, and 256nm respectively) and distinguishes (177) from pyrazines (λ_{max}, *c.a.* 280nm),[148] pyridazines (two or more bands at longer wavelength)[151] and valence bond isomers (λ_{max} *c.a.* 220nm).[192]



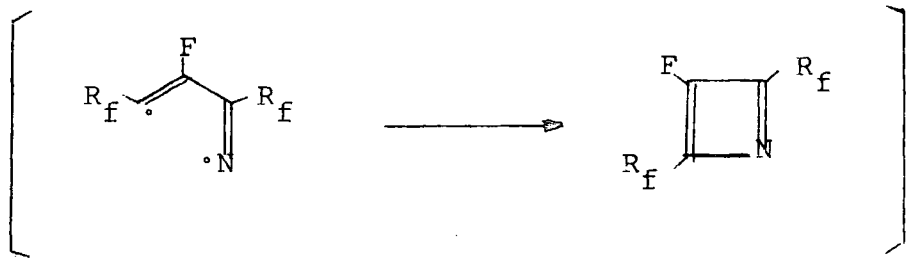
(164) (177) 31% (178) 8%

(R_f = $CF(CF_3)_2$) R_fCN + $R_fC{\equiv}CF$

(46) 12.3% (179) 2.4%



(180) 5.3% (182) 1.2%



(181a) (181)

The ^{19}F n.m.r. spectrum (177) shows two characteristic chemical shifts at 61.7 and 159 ppm., corresponding to the ring fluorine at the 6-position and the tertiary fluorine on the isopropyl group at the 5-position (the corresponding fluorine in perfluorotetraisopropylpyrimidine[113]; 149 ppm.).

TABLE 6.1 Spectroscopic data of (177)

^{19}F n.m.r. spectrum (neat; ext. ref. $CFCl_3$)

Shift (ppm.)	Structure	Intensity
61.7	S	1
75.5	D (J=3.7Hz)	6
77.6	T (J=7.4Hz)	6
78.9	Sept (J=2.8Hz)	6
159.0	M	1
184.3	M	1
188.5	M	1

I.R. spectrum

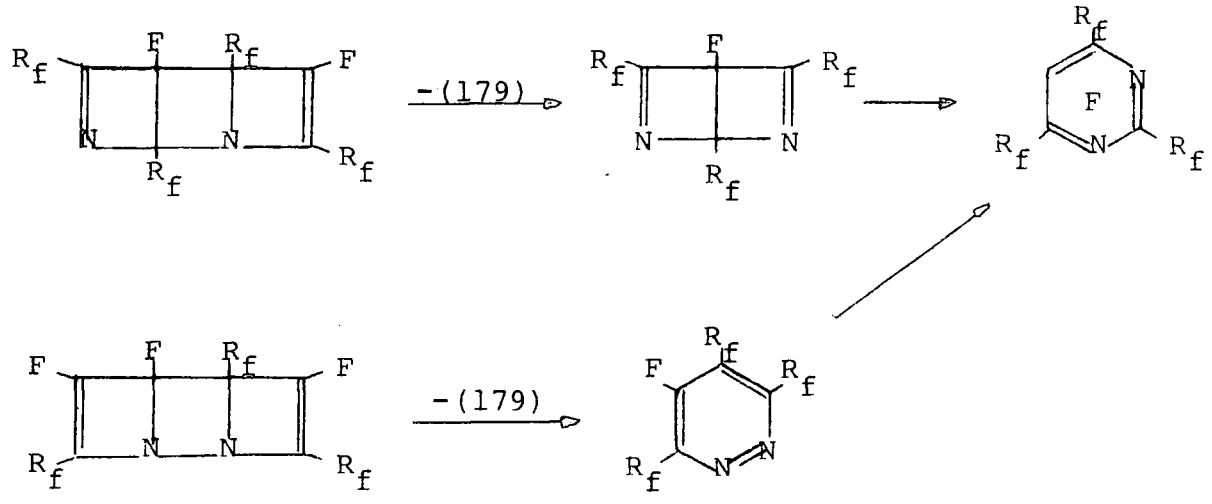
1500 cm^{-1}, 1600 cm^{-1}, 1725 cm^{-1}

UV spectrum

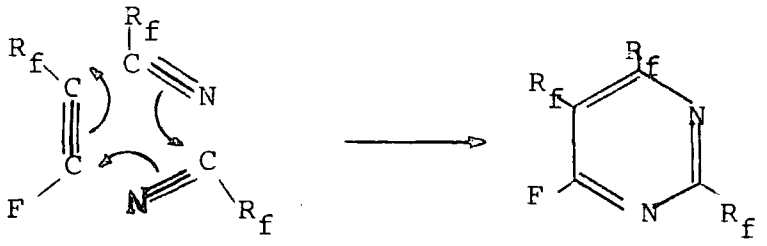
λ_{max} 256 nm ε = 7100

222 nm(sh) ε = 4400

The dimer (180) provides clear evidence of the cyclic intermediate (181) and accounts for the formation of (46) and (178) (see Chapter Seven 4(A)). However, formation of (177) is less clear since loss of (179) does not occur from (180) under these conditions. Other dimers of (181) could lead to a pyrimidine with perfluoroisopropyl groups at the different positions, even *via* rearrangement.[148] It is probable that this process involves [2 + 2 + 2] cyclization of the nitrile (46) and the acetylene (179), presumably catalyzed by glass surface as shown below. Fluorinated nitriles undergo trimerization to form 1,3,5-triazines under high pressure and temperature.[153] Reaction of nitriles and acetylide salts



$(R_f = CF(CF_3)_2)$

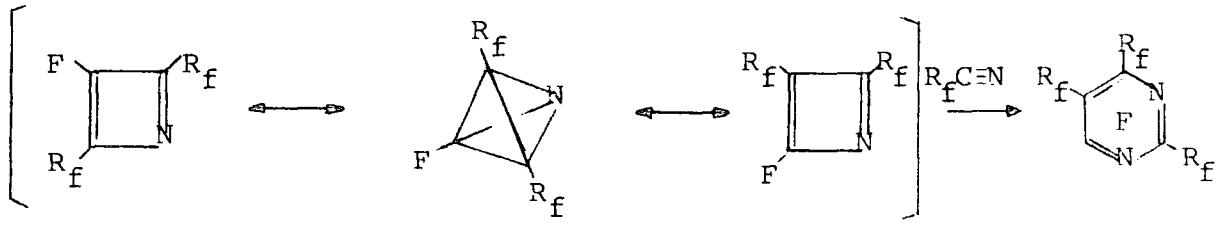


(177)

lead to formation of 2,4-disubstituted pyrimidines and 2-substituted pyridines which also require the utilization of elevated temperatures and pressures.[154] In addition, nitriles, including fluorinated derivatives such as (46)[212,213] undergo [4 + 2] cycloaddition with dienes in gas phase to afford 2-substituted pyridines. It was suggested that elevated temperature and Lewis acid-induced polarization of cyano-groups lower the energy of transition state for cycloaddition.[214]

An alternative possibility for the formation of (177) may involve rearrangement of (181) to (184) *via* an azatetrahedrane (183), which then reacts with the nitrile (46).

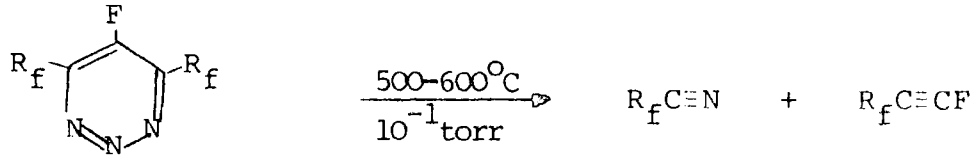
However, the process appears unlikely since any dimers were not observed which could arise from (184). Other products could stem from the fragmentation of the azete (181).



(181) (183) (184) (177)

(B) Flash Pyrolysis

The triazine (164) gave only two products (46) and (179) quantitatively on flash pyrolysis above 500°C without formation of any dimers or an azatetrahedrane (183). These products could be derived from simple fragmentation of either (164) or the diradical (181a) without formation of (181).



(164) (46) (179)

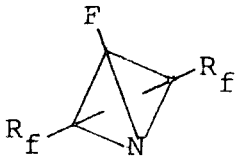
$(R_f = CF(CF_3)_2)$

In addition no scrambled acetylenes such as (45) and (185) were obtained, suggesting that the species (183) could not be involved in the process. However, this process provides a clean preparative method of a fluoroacetylene in high yield

for further investigation.

$R_fC{\equiv}CR_f$ (45)

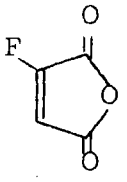
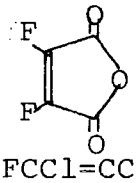
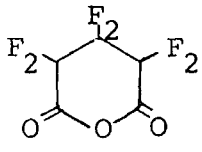
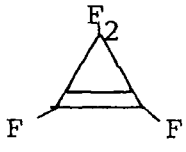
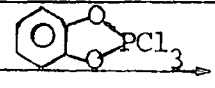
$FC{\equiv}CF$ (185)



(183)

Other preparative methods of fluoroacetylenes are symmarized in Table 6.2.

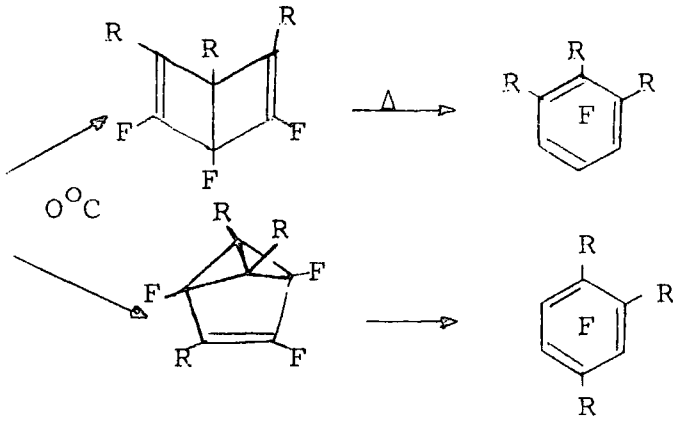
TABLE 6.2 Synthesis of fluoro acetylenes

Process	Lit
 $\xrightarrow[5\text{-}7\text{mmHg}]{600^{\circ}C}$ $FC{\equiv}CH + CO_2 + CO$ (quant.)	155
$F_2C{=}CH_2 \xrightarrow[-78^{\circ}C]{RLi} [FLiC{=}CH_2] \longrightarrow [FC{\equiv}CH]$ (90%)	156
 $\xrightarrow{600^{\circ}C}$ $FC{\equiv}CF + FC{\equiv}CCOF + CO_2{+}CO$	157
$FCCl{=}CClF \xrightarrow{PhLi} [LiCF{=}CClF] \longrightarrow [FC{\equiv}CF]$	158
$CF_2Br\text{-}\underset{H}{C}Br\text{-}\underset{Br}{C}F_2 \xrightarrow[-196 \text{ to } 20]{AlBr_3} CF_3\text{-}CBr{=}CFBr \xrightarrow[\text{reflux}]{Zn/Dioxane} CF_3C{\equiv}CF$	159
 $\xrightarrow[420^{\circ}C/1\text{-}2\text{mmHg}]{KF}$ $[CF_2{=}CFCF_2COF] \longrightarrow CF_3CF{=}CFCOF$ (26%)	160
$\xrightarrow{NaOH} CF_3CF{=}CFCO_2Na$ (86%) $\xrightarrow{220\text{-}240^{\circ}C} CF_3C{\equiv}CF$ (26%)	
 $\xrightarrow{h\nu}$ $CF_3C{\equiv}CF$	161
$t\text{-}BuCOCH_2Br \xrightarrow{KF} t\text{-}BuCOCH_2F \xrightarrow{PCl_3}$ 	162
$tBu\text{-}CCl{=}CHF \xrightarrow{-HCl} t\text{-}Bu\text{-}C{\equiv}CF$	
$CF_2{=}CFCl \xrightarrow[-MF]{ArM} ArCF{=}CFCl \xrightarrow{RLi} [ArCF{=}CFLi] \longrightarrow ArC{\equiv}CF$ (~90%)	163
$CFH{=}CCl_2 \xrightarrow[10^{-3}\text{Torr}]{KOH\ 125^{\circ}C} FC{\equiv}CCl$	164
$CF_3\underset{X}{C} = CX_2 \longrightarrow CF_3C{\equiv}CX$ (X=Cl, Br)	165
 $\rightleftharpoons [CF_2{=}CF\text{-}CF{=}CF_2] \longrightarrow CF_3C{\equiv}CCF_3$	166

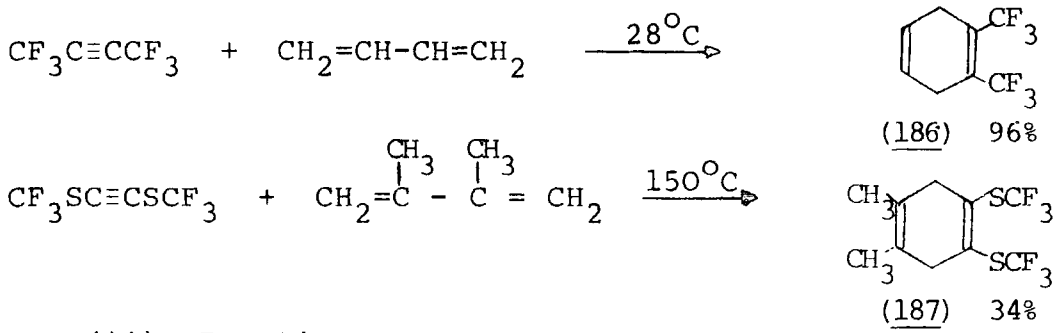
(C) Reactions of perfluoro-3-methylbut-1-yne

(i) Introduction

Fluoro-acetylenes are highly reactive because of the high energy of the systems attributable to repulsion between electrons and the nonbonding electron pairs on fluorine.[167,168,169] In fact monofluoro-[155] and difluoro-[157] acetylenes polymerize spontaneously at room temperature and tert-butyl fluoroacetylene readily forms trimers[162] as shown below:

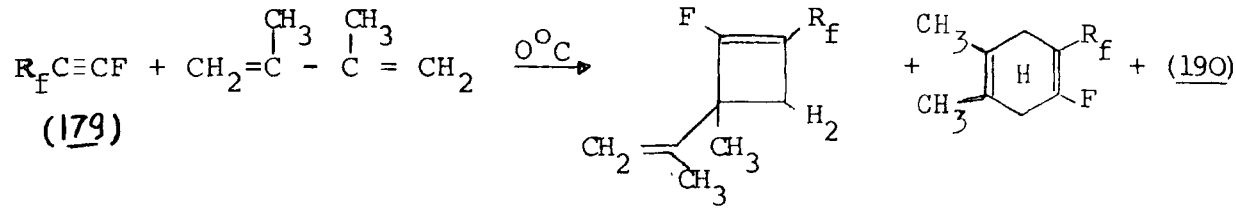


In contrast, perfluoropropyne is considerably more stable.[159] Perfluorinated acetylenes undergo cycloaddition reactions to yield adducts such as (186)[170] and (187).[171]



(ii) Reactions

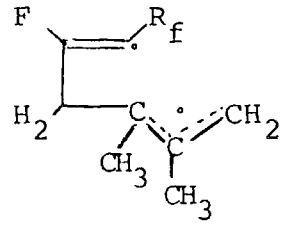
Thermal oligomerization of (179) was attempted at 100°C without success, which demonstrates greater stability analogous to perfluoropropyne. The acetylene (179) also did not react with the nitrile (46) at the same temperature, but readily with 2,3-dimethylbuta-2,3-diene even at 0°C.



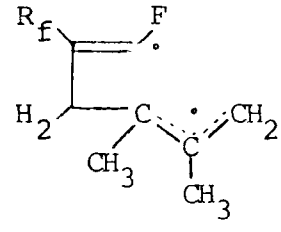
(179) (188) (189) (190)

72.3% 18% 9.8%

The products were two 1:1- and four 2:1-adducts, where the latter were not characterized. The predominance of [2+2] cycloaddition product (188), over expected [4+2] adduct (189) by the analogy with (186), shows high reactivity of (179). The [2+2] cycloaddition adducts have been obtained by the reaction of fluorinated alkenes with dienes at much higher temperature, which is one of the most unusual aspects of fluorocarbon chemistry since the reaction is forbidden as the thermally induced concerted process.[172] A free radical process could account for the orientation of the product (188) by the analogy with fluorinated alkenes.[173,174] The inter-



(191a)



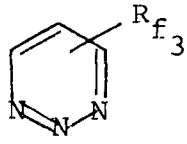
(191b)

mediate diradical (191b) is expected to be more stable than (191a) because of electron-donating nature of fluorine by resonance.[39]

An attempt to obtain an adduct of perfluorisobutyronitrile (46) with 2,3-dimethylbuta-1,3-diene was made at 100°C without success, though trifluoromethyl nitrile gave 2-trifluoromethyl pyridine with buta-1,3-diene for short contact time at 400°C and an adduct was proposed as an intermediate.[175]

6.5 Perfluoro Trisisopropyl-1,2,3-Triazine

Static (at 200°C for 1.5 hr.) as well as flash (500°C) pyrolyses yielded perfluoro-isobutyronitrile (46) and perfluoro-2,5-dimethyl-hex-3-yne (45) quantitatively, *i.e.*, an analogous result to that obtained with perfluorotrisisopropyl-1,2,4-triazine (44).[11] It is not possible to confirm whether these products arose from simple [2+2+2] fragmentation of (165) or *via* a cyclic intermediate (192).



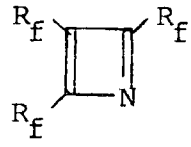
(165)

$$\xrightarrow[\text{or } 600^{\circ}C\ 10^{-1}\ \text{Torr}]{200^{\circ}C \times 1.5\ \text{hr.}} R_fC{\equiv}CR_f + R_fCN$$

(45) (46)

(quant.)

($R_f = CF(CF_3)_2$)

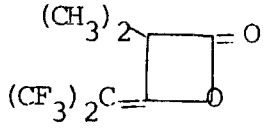


(192)

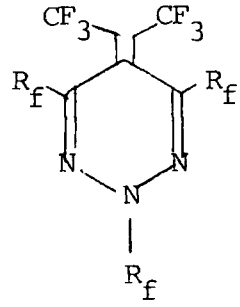
6.6 Perfluoro-2,4,6-Trisisopropyl-5-Isopropylidene-1,2,3-Triazacyclohexa-3,6-diene

The synthetic routes to fluorinated allenes are limited, which may be summarized in Table 6.3. Starting materials are mainly fluorinated acetylenes or toxic perfluoroisobutene.

TABLE 6.3 Synthesis of fluorinated allenes

Process (yield)	Lit
$CF_3C{\equiv}CF \xrightarrow[165^oC/5min.]{C_5F} CF_2{=}C{=}CF_2$ (86%)	159
$CF_3CH{=}CR_2 \xrightarrow{Br_2} CF_3CHBrCR_2Br \xrightarrow{KOH} CF_3CBr{=}CR_2$ (80%) (14%) $\xrightarrow{BuLi} CF_3CLi{=}CR_2 \xrightarrow{\Delta} CF_2{=}C{=}CR_2$ (28%) (R=H, CH_3)	176,177
$CF_3C{\equiv}CCF_3 \xrightarrow[250^oC]{R_fI} CF_3CI{=}C(CF_3)R_f$ 55-67% $\xrightarrow[200^oC]{Cu} CF_2{=}C{=}C(CF_3)R_f$ (95%) (R_f=C_2F_5, C_3F_7)	178
$(CF_3)_2C{=}CF_2 \xrightarrow{H_2O} (CF_3)_2CHCO_2H \xrightarrow{P_2O_5} (CF_3)_2C{=}C{=}O$ (94%) $\xrightarrow{P(OC_2H_5)_3} (CF_3)_2C{=}C{=}C(CF_3)_2$	179,180
$\xrightarrow{(CH_3)_2C=C=O}$  $\xrightarrow[-CO_2]{\Delta} (CF_3)_2C{=}C{=}C(CH_3)_2$	181
$(CF_3)_2C{=}CF_2 \xrightarrow[r.t.]{CHRCO_2Me/C_3F} (CF_3)_2C{=}C{=}C(CO_2Me)R$ (43-63%.) (R=Ph, CO_2Me)	182
$(CF_3)_2CFCH_2CF_2I \longrightarrow (CF_3)_2C{=}C{=}CF_2$ (35%)	183
$(CF_3)_2C(OH)C{-}C{\equiv}CH \xrightarrow{SF_4} (CF_3)_2C{=}C{=}C(H)F$	184
$(CF_3)_2CO + Ph_3P{=}C{=}C(OEt)_2 \longrightarrow (CF_3)_2C{=}C{=}C(OEt)_2$	264

Static pyrolysis of the unusual compound (166) at 350°C for 4 hrs. gave mainly four products, which are perfluorinated-allene (193), -diallene (194), -allene acetylene (195) and -isobutyronitrile (46). The structure of (193) was



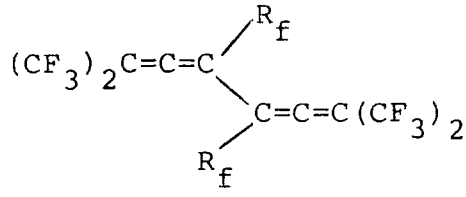
(166)

$(R_f = CF(CF_3)_2)$

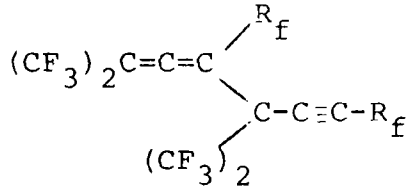
$\xrightarrow[3\ hrs.]{350^{\circ}C}$

$(CF_3)_2C{=}C{=}C(R_f)_2 + R_fCN$

(193) 60% (46) 68%

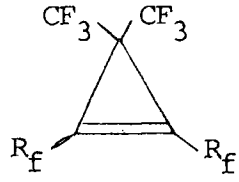


(194) 13%

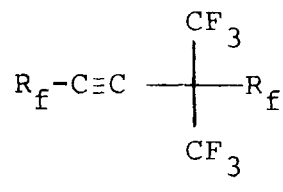


(195) 12%

distinguished from other candidates, *i.e.*, cyclopropene (196) and acetylene (197) by the characteristic absorption (2005 cm^{-1}) in the i.r. spectrum and ^{13}C chemical shift of the central carbon (202.9 ppm.). The spectroscopic data of (193) as well as (45) were, in turn, used to confirm the structures of (194) and (195).



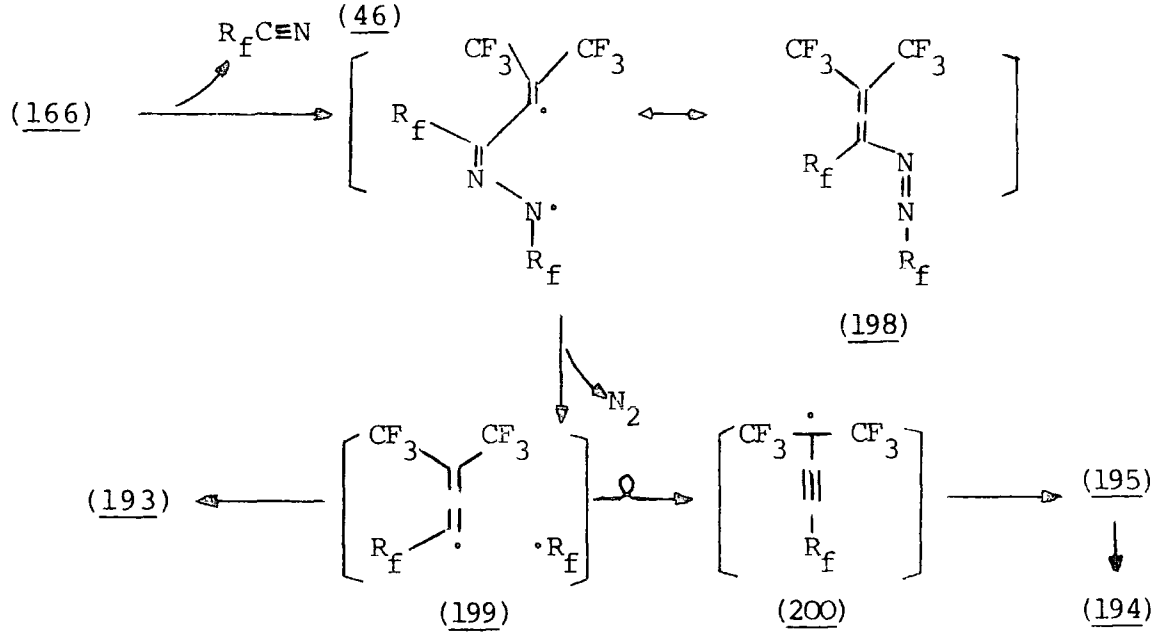
(196)



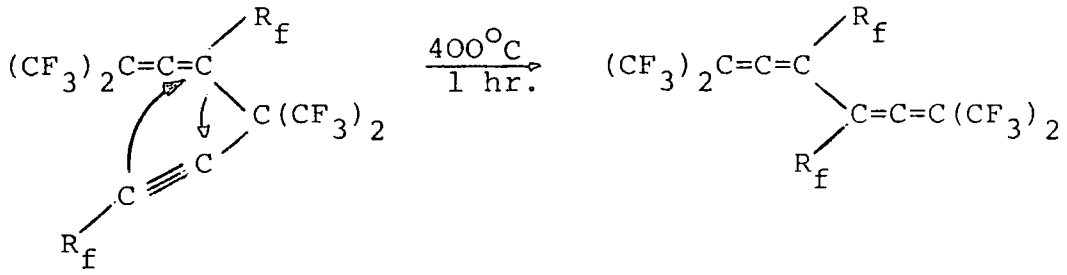
(197)

The mechanism of the formation of these products could be summarized in Scheme 6. Elimination of (46) from (166), followed by rearrangement leads to azo-derivative (198).

Scheme 6



The compound (198) extrudes nitrogen, to form radicals, since fluorinated azo-compounds are usually not stable above 300°C.[185] Simple coupling reaction gives (193), whereas rearrangement of the radical (199) forms acetylene radical (200), which then affords (195) by coupling reaction with (199). However, it is not certain whether the diallene (194) arises directly from (199) since the compound (195) was readily isomerized to (194) quantitatively at 400°C. This process could involve [1,3] shift of carbon skelton.[186] There are few reported examples of analogous rearrangement, which are thiophenoxybut-2-yne,[187] trimethylsilylprop-1-yne,[188] and propyne.[189] The reason could be attributable to the fact that thermal concerted [1,3] shift is symmetry forbidden.



(195) (194)

In addition, there can be no thermodynamic driving force for rearrangement of acetylenes to allenes since the process is endothermic[190] (at 298K, ΔG_f°(propyne) = 46.3 Kcal/mole, whereas ΔG_f°(allene) = 48.4 Kcal/mole). However, the conversion of (195) to (194) forms a conjugated system and may remove steric constraints. It could be these factors that provide the driving force for the reaction. Furthermore, a "trans" bending of an acetylene leads to a substantial decrease in the LUMO of the acetylene, which favours the interaction with HOMO in nucleophiles and then its distortion in the transition state.[191] This accounts for the common intramolecular pericyclic reaction of acetylenes to allenes.[186]

CHAPTER SEVEN

PHOTOLYSIS

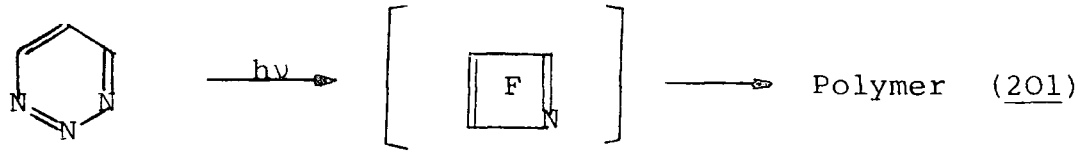
7.1 Introduction

Photochemical elimination of nitrogen from 1,2,3- and 1,2,4-triazines occurs with the formation of acetylenes and nitriles as is the case in corresponding pyrolysis process. However, benzoazetes were synthesized by a photochemical process.[10] Fluorinated pyridazines were isomerized to the corresponding pyrazines[192,193] and para-bonded intermediates have been isolated from a number of fluorinated derivatives.[194] It was from a para-bonded species that elimination of $R_fC{\equiv}N$ occurred to give a fluorinated azete.[15]

In this chapter, attempts are discussed for the photochemical generation and trapping of azetes from fluorinated-1,2,3-triazines. Also described are attempts to observe directly the intermediates.

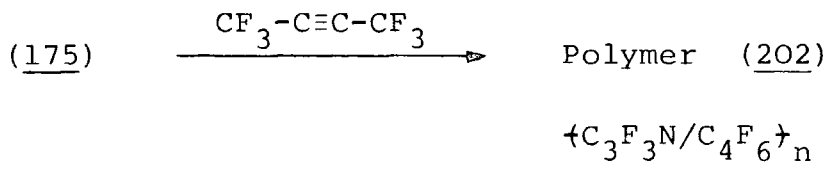
7.2 Trifluoro-1,2,3-triazine

Photolysis of trifluoro-1,2,3-triazine (163) at 253.7nm provided a polymeric product on the surface of quartz tube. The elemental analysis of the polymer (201) corresponded approximately with loss of nitrogen from (163) and the i.r. spectrum indicates that it contains unsaturated sites but not nitrile groups. Therefore the polymer (201) might be poly-adduct of the azete (175). Nevertheless, the structure remains ambiguous since (201) did not dissolve in usual organic solvents, presumably because of crosslinking along the chain.

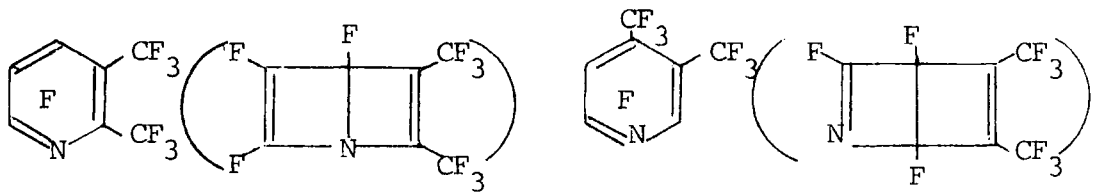


(163) (175) $+C_3F_3N+_n$

An attempt to trap the intermediate (175) with hexafluorobut-2-yne led to a modified polymer, whose mass spectrum showed a major peak at 269 corresponding to a 1:1 adduct (202). Indeed, a liquid product was obtained, using a much larger vessel, which is a 1:1 adduct detected by mass spectroscopy.



This could be pyridines (or their valence bond isomers) (203a) and (203b), but the exact structure is not known.



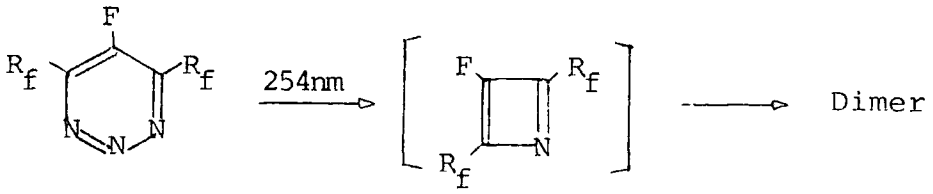
(203a) (203b)

7.3 Perfluoro-4,6-Bisisopropyl-1,2,3-Triazine

(A) Formation of a Dimer of the Azete

When perfluoro-4,6-bisisopropyl-1,2,3-triazine (164) was photolyzed in liquid phase, a dimer (180) of the corres-

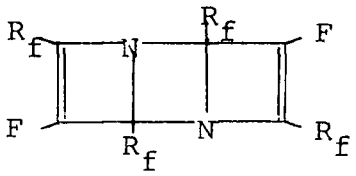
ponding azete was formed quantitatively, to give clear evidence for the cyclic intermediate (181). The dimer (180) was also obtained in vapour phase photolysis. The structure



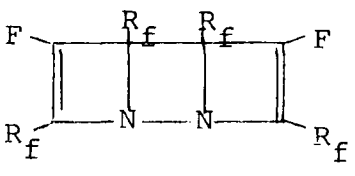
(164) (181) (180)

(R_f=CF(CF_3)$_2$)

of (180) was tentatively assigned to be either (180a) or (180b) on the basis of the ^{19}F n.m.r. spectrum, Table 7.1,



(180a)

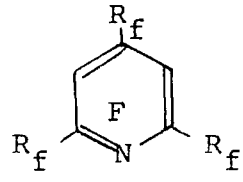


(180b)

which shows two fluorines at vinylic sites (111-114 p.p.m.). In order to distinguish between the two structures, pyrolysis and photolysis of (180) were attempted. The dimer (180) remains unchanged on prolonged photolysis and pyrolysis below 300°C. However, above 350°C, (180) could be pyrolyzed within 2 hrs. to give perfluorinated pyridine (204)[195] and perfluoroisobutyronitrile (46) quantitatively. This process could proceed *via* ring-opening to the 1,4-diazocine (205), followed

TABLE 7.1 ^{19}F n.m.r. spectrum of (180)

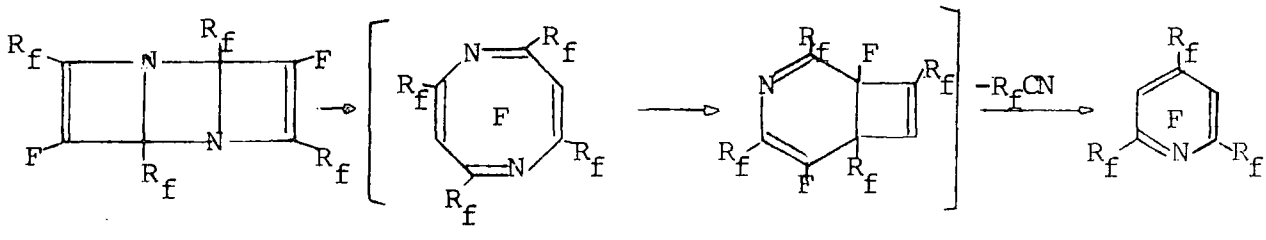
Chemical shift (ppm)	Structure	Intensity
76.4	S	6
77.2	S	12
77.6	S	6
112.4	D (J = 56.2 Hz)	1
113.0	D (J = 56.2 Hz)	1
185.5	M (J = 5.6 Hz)	2
185.8	D (J = 5 6 Hz) of Sept (J=5.6Hz)	2

(180) $\xrightarrow[2\ hrs.]{350^{o}C}$  + $R_fC \equiv N$

(204) (46)

by ring-closure to the bicyclic isomer (206) and elimination of (46), indicating clearly that the structure is (180a).

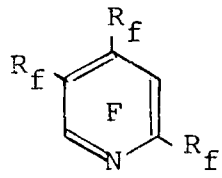
Scheme 7.1



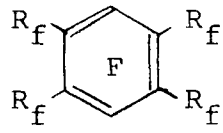
(180) (205) (206) (204)

(R_f=$CF(CF_3)_2$)

Hence the dimer (180b) could lead to a different pyridine (207) or a benzene (208) by analogous mechanism.



(207)



(208)

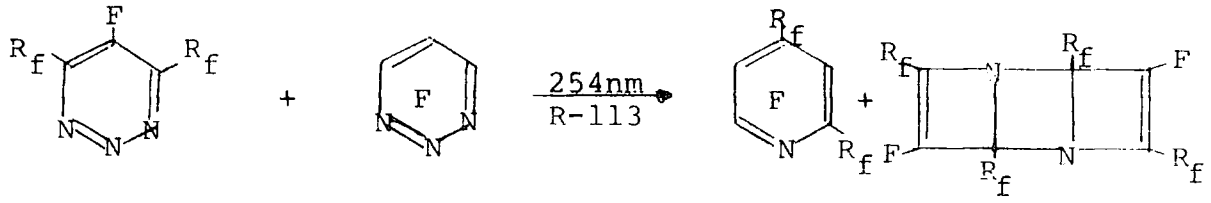
Hexaphenyl-1,4-diazocine was converted to pentaphenylpyridine and benzonitrile,[14] 1,2-diazocine to benzene, pyridine and cyanuric acid,[196] and hexamethyl-1,2-diazocine to hexamethyl benzene[197] on pyrolyses.

It is noteworthy that the usually less stable tricyclic valence isomer (180) becomes thermodynamically more favoured than the corresponding eight-membered ring.[198] Analogous phenomenam has been observed recently in a cyclooctatetraene valence isomer with bulky substituents on the adjacent carbons.[199] It seems clear that the stability of (180) is attributable to the steric interaction between the perfluoroisopropyl groups. In fact the interaction reflects the two sets of non-equivalent trifluoromethyl groups observed in the ^{19}F n.m.r. spectrum and is consistent with so-called "perfluoroalkyl effect"[200] where the groups exert profound influences on the stability of strained small ring systems.[101,201]

(B) Trapping of the Azete

(i) Trifluoro-1,2,3-Triazine

Co-photolysis of (164) with trifluoro-1,2,3-triazine was attempted in liquid phase, yielding a fluorinated pyridine (209)[205] and the dimer (180), together with trifluoro-1,3,5-triazine (210)[206] and polymer.



(1 : 3.3) (5.7 : 1)

(164) (163) (209) (180)

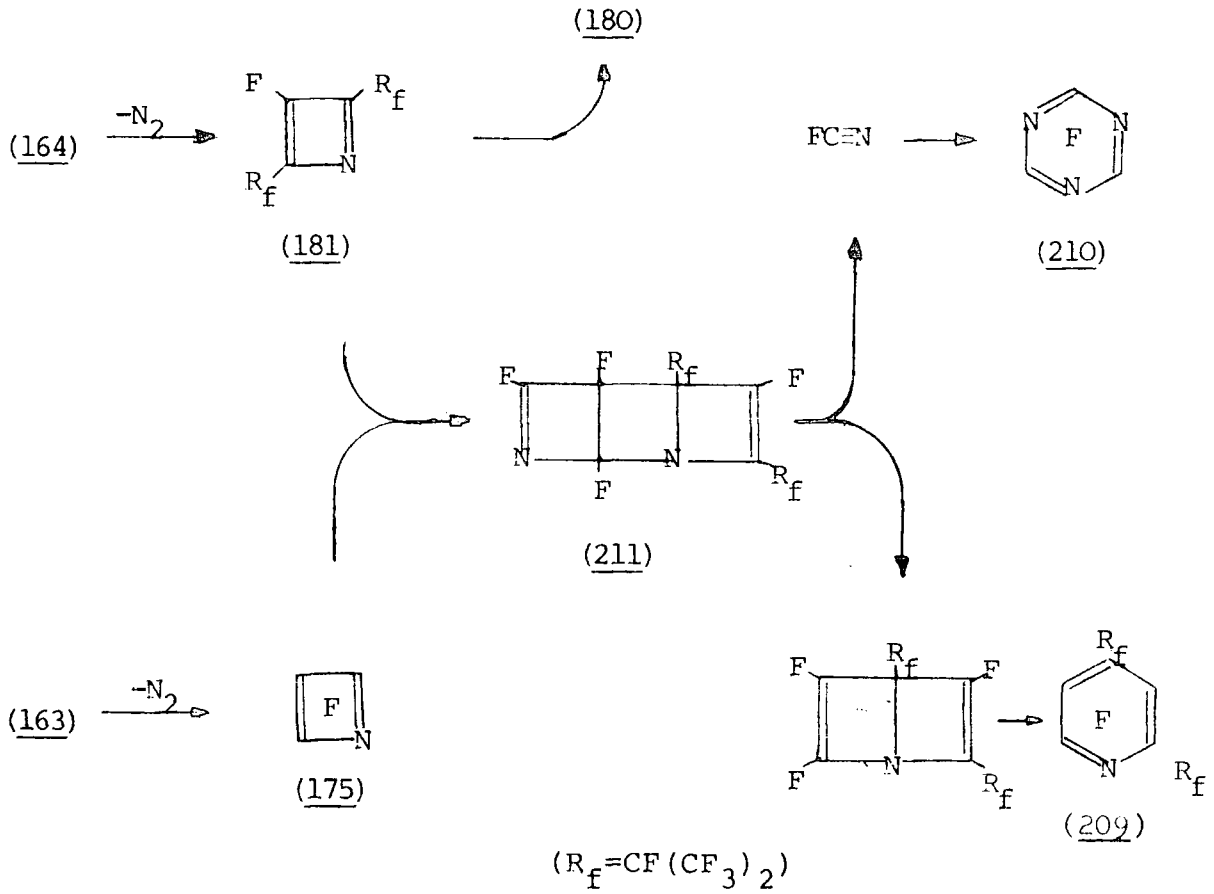
+ (210)

+ polymer.

These products could stem from the cross-dimer (211) between azetes (181) and (175) as shown in Scheme 7.2.

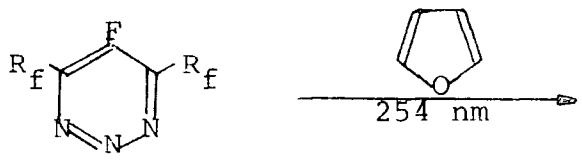
Since photolysis of (164) in the presence of tetrafluoropyridazine led to the dimer (180) in high yield, this might exclude possibility that (181) reacts with (163) directly. In addition the triazine (210) was not detected on the photolysis of (163). Thus, the product (209) provides the first clear evidence that a monocyclic azete has been trapped.

Scheme 7.2



(ii) Furan

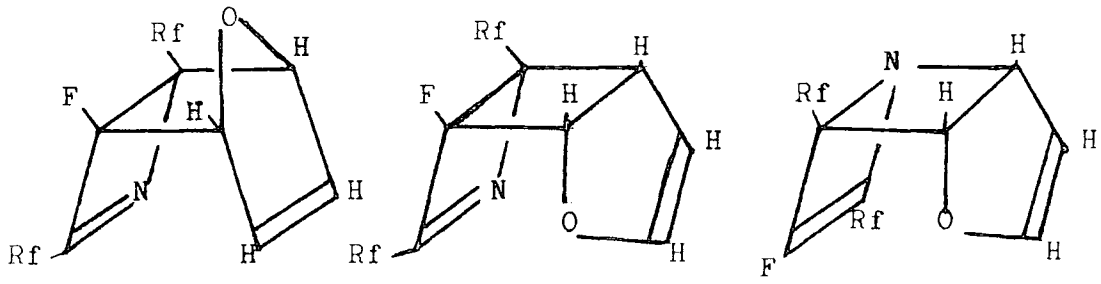
Photolysis of the triazine (164) was carried out in the presence of excess furan in liquid phase, to give three 1:1 adducts (212), (213) and (214). Their structures were assigned on the basis of their n.m.r. spectra by the comparison with those in adducts of fluorinated cyclobutadienes and Dewar benzenes with furan[202, 203] and cyclopentadiene-dimer.[204] The tertiary fluorine chemical shift (160 p.p.m) in (212) is consistent with endo-adducts[202] and much lower than the shifts (*e.a.* 190 p.p.m.) expected for exo-forms.[204] The same shift also indicates that the fluorine in (213) might be at the β-position to oxygen since the



(164)

adducts (212), (213) (214)

34% 21% 13%

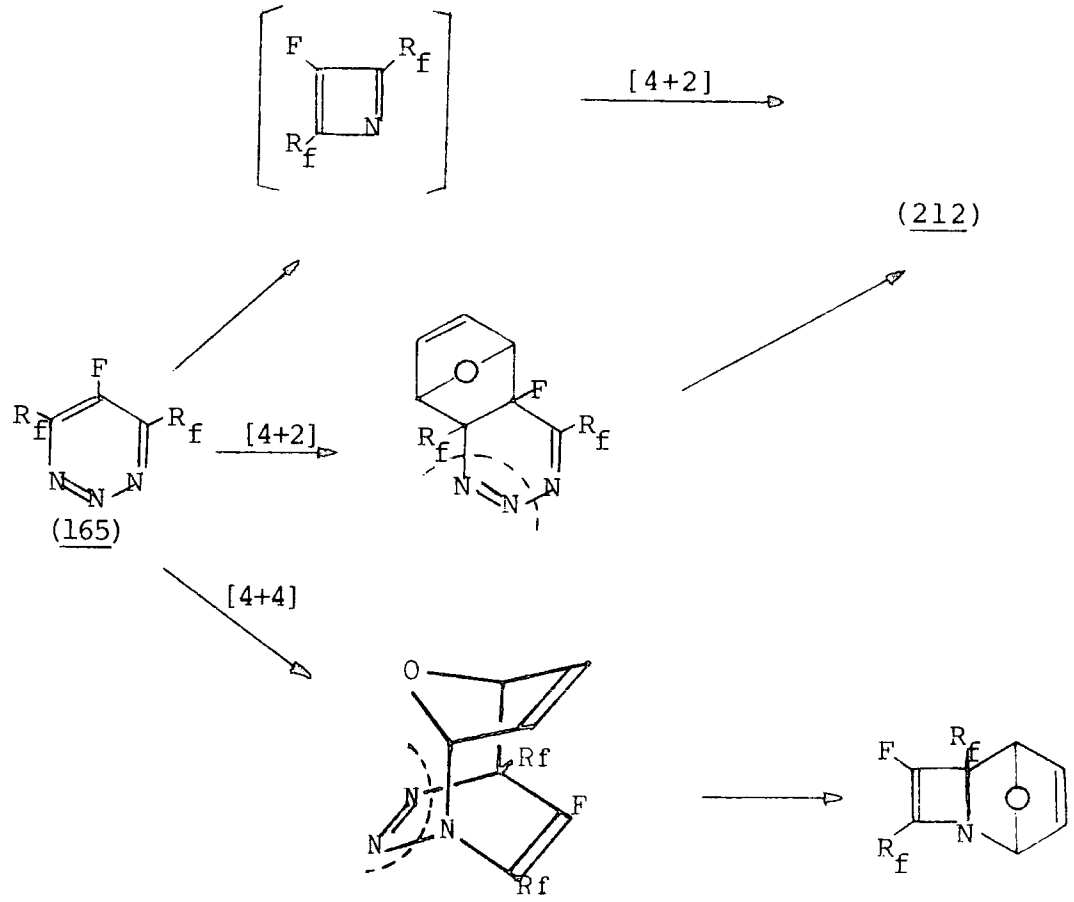


(212) (213) (214)

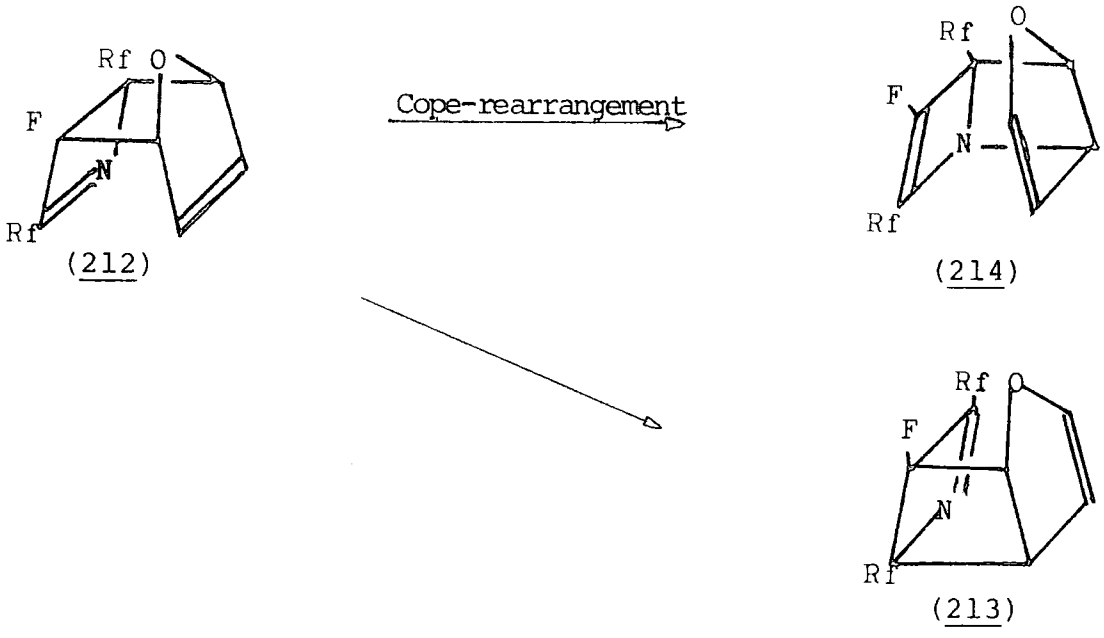
(R_f=$CF(CF_3)_2$)

value is lower than an adduct without oxygen (*c.a.* 10 p.p.m.). The structure of (214) is based on the existence of vinylic fluorine (97.3 p.p.m.) and two methine protons in considerably high field, the latter suggesting that they are on the carbons at the α-position to heteroatoms.

Formation of (212) is most readily explained by trapping of the azete (181) with furan, since photochemical [4+2] cycloaddition is symmetry-forbidden and possible [4+4] cycloaddition leads to a different adduct. In addition, the triazine (165) does not react with 2,3-dimethylbutadiene (see Chapter Eight) which argues against thermal [4+2] cycloaddition.



Other adducts (213) and (214) could be formed by Cope-rearrangement of (212). A photochemical [4+4] cycloadduct of furan with benzene[250(c)] underwent Cope-rearrangement to



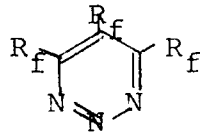
give a product with an analogous structure to (213) and (214).

(iii) Other Attempts

The triazine (164) was photolyzed in the presence of hexafluorobut-2-yne, perfluoro-isopropylacetylene (179) and perfluoroisobutyronitrile (46) to yield the dimer (180) of the azete with none of the adducts. An attempt was also made to trap the azete (181) with tetramethylethylene, giving the dimer (180), although a small amount of an adduct was detected (by mass spectroscopy). Further investigation was not made.

7.4 Perfluoro-Trisisopropyl-1,2,3-Triazine

Photolysis of perfluoro-trisisopropyl-1,2,3-triazine (165) at 254 nm led to formation of perfluoro-2,5-dimethylhex-3-yne (45) and perfluoroisobutyronitrile (46) without re-arrangement to other triazines, in contrast to perfluorotris-isopropyl-1,2,4-triazine[11] which gave the corresponding 1,3,5-



(165)

$$\xrightarrow{254nm} \quad R_fC{\equiv}CR_f \quad + \quad R_fC{\equiv}N$$

(45) (46)

(R_f=$CF(CF_3)_2$)

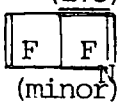
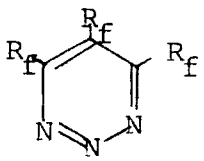
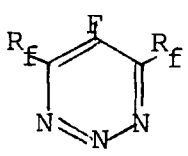
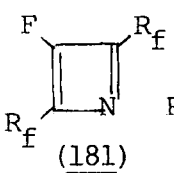
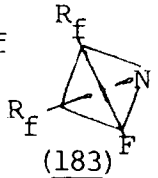
triazine as well as (45) and (46) on photolysis.[11] It is not possible to reveal the process as in the case of pyrolysis of (165).

7.5 Low Temperature Photolysis

(A) Observation of the Intermediates

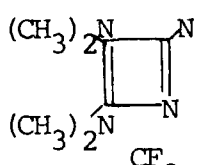
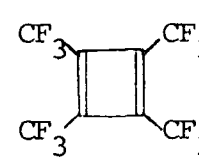
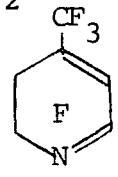
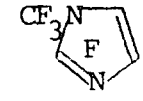
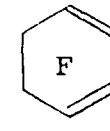
Photolyses of fluorinated-1,2,3-triazines (163), (164) and (165) were carried out at cryogenic temperature (77K) on a KBr disk without matrix material, in order to observe the cyclic intermediates directly. The i.r. spectra of the photolysates were recorded at the same temperature and then, the mass spectra were obtained at different temperatures during warming up to room temperature by connecting the apparatus directly to the mass spectrometer. The first parent peak appeared at *c.a.* -40°C and then peaks with higher molecular weights were observed gradually. It is not possible to say with accuracy what temperature the other peaks appeared and in the Table 7.2, these are indicated as (high temp.).

TABLE 7.2 Low Temperature Photolysis

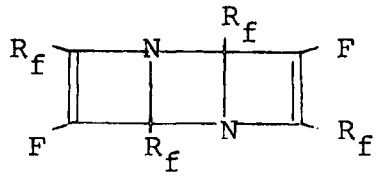
Starting Material	I.R. New Absorptions > 1350 cm^{-1}	Mass Spectra detected m/e	Proposed Structure
	1645 1675	107	 (175)
	1720(vw) 1760(vw)	169 (high temp.)	 (minor) (215)
	2160	343(M^+-19) (high temp.)	$R_fC{\equiv}CR_f$ (45)
	2230	176 (M^+-19)	$R_fC{\equiv}N$ (46)
 (164)	No observable absorption	407	 (181) (minor)  (183)
		745(M^+-69) (high temp.)	Dimers (major)

Perfluorotrisisopropyl-1,2,3-triazine (165) undergoes fragmentation to the acetylene (45) and the nitrile (46) even at 77K. However, a product from trifluoro-1,2,3-triazine (163) shows absorptions at 1645 and 1675 cm^{-1}, which are consistent with C=C and C=N bonds under conjugation as shown in Table 7.3. More significantly, the molecular weight of the product is 107 which was observed as parent peak and corresponds to the cyclic intermediate (175) since the starting material (163) shows clear parent peak at 135. The azete (175) could be stable up to *c.a.*-30∿-40°C where the mass spectrum were obtained. Minor by-product may be a Dewar pyridine (215) which is speculated by molecular weight (169) and weak absorptions in the i.r. spectrum of the photolysate, without further investigation.

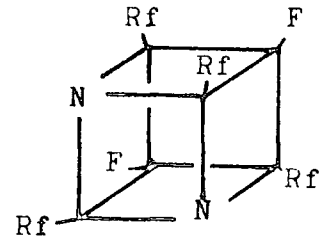
TABLE 7.3 I.R. Absorptions

Compound (lit.)	Absorption	Compound (lit)	Absorption
 10	1630	 66	1700
 206	1750 1735	 208	1710 1630
$CF_3N{=}C(F){-}C(F){=}NCF_3$ 207	1650	 209	1797
$CF_2{=}CF{-}CF{=}CF_2$ 209	1770	 209	1750 1710

For perfluorobisisopropyl-1,2,3-triazine (164), the i.r. spectrum of the photolysate was similar to that observed for the dimer (180) and the latter spectrum has been recorded at 77K, *i.e.*, identical conditions, but at these low temperatures there is none the less a detectable weak absorption in the C=C and C=N regions. However, no absorption in this region was detectable for the product from (164). At *c.a.* -40°C, a mass spectrum appeared with a parent peak at 407, *i.e.*, corresponding to the azete (181). Since it is not possible to be confident about the detection of C=N and C=C bonds in this species, it is not certain whether this monomeric species has the azete or even an azatetrahedrane structure (*N.B.* the triazine (164) shows clear parent peak at 435). At higher temperatures, the mass spectrum indicated a dimer similar to the spectrum of (180). The dimer could even have a diazacubane structure (216).



(180)

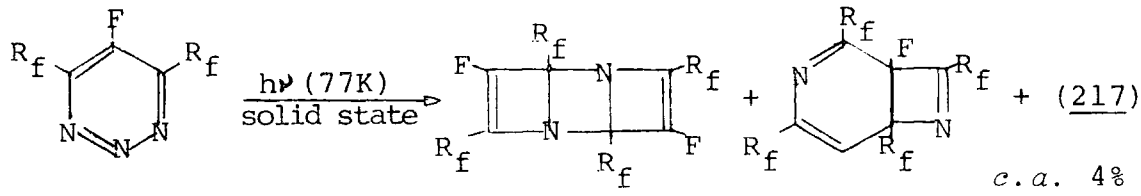


(216)

(B) Attempted Isolation of Photolysates

Preparative scale photolysis of (164) was attempted in order to isolate the product, observed at 77K (see (A)). Solid state photolysis of thin film of (164) at 77K gave a mixture of three dimers, which showed almost identical mass

spectra. A major component was the dimer (180).



(164) (180) 70% (206) 23% *c.a.* 4%

(R_f = $CF(CF_3)_2$)

Another dimer was tentatively assigned to (206). This follows from spectroscopic data as shown in Table 7.4. It shows one fluorine at vinylic region and five fluorines in high field (tertiary fluorines), one of which is distinct from others and corresponds to the bridgehead fluorine. In addition, the i.r. spectrum indicates the existence of three different unsaturation,

TABLE 7.4 Spectroscopic data for (206)

^{19}F N.m.r. spectrum

	Shift (p.p.m.)	Structure	Intensity	Assignment
	76-78	M	24	2b,4b,6b,8b
2a 2b $CF(CF_3)_2$ 28a 8b	105.3	D broad (J=74 Hz)	1	5
	161.7	S broad	1	1
	182.0	S broad	2	2a, 4a, 6a, 8a.
	187.0	S broad	1	
	189.0	S broad	1	

I.R. SPECTRA (cm^{-1})

1535, 1600, 1715 cm^{-1}

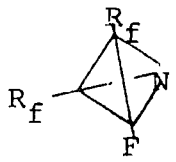
(C=N) (C=N) (C=C)

and is in accord with the structure (206). Other weak peaks were also observed which may be attributable to the other dimer (217).

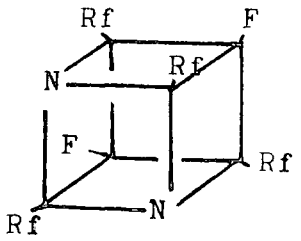
Photolysis of the triazine (164) in organic glass (-30°C) was also carried out, giving a mixture of the same dimers.

The i.r. spectrum of the mixture, observed at 77K, is similar to that of the photolysate formed on KBr plate but shows detectable absorption in the region of unsaturation.

Therefore, it is concluded that the product, observed on KBr plate at 77K, does not survive on warming. The structure may be an azatetrahedrane (183) or a diazacubane (216).



(183)

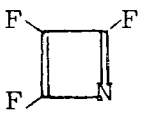


(216)

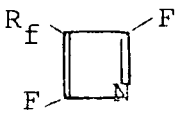
Temperature dependence of products have been observed in the photolytic formation of 1,2-diazocine from a tetracyclic azo-compound, where low temperature (-50°C) favours 1,2-diazocine rather than valence isomers of benzene.[196] This was attributed to different modes of bond cleavage in the diazo-compound.

7.6 On the feature of Azetes (Conclusion)

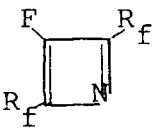
Azetes have been observed and trapped as dimers and adducts which are discussed in this chapter, elucidating their features. Fluorinated azetes, so far obtained are (175), (80) and (181) but not (192). Theoretical calculation suggests



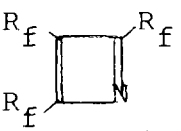
(175)



(80)[15]



(181)

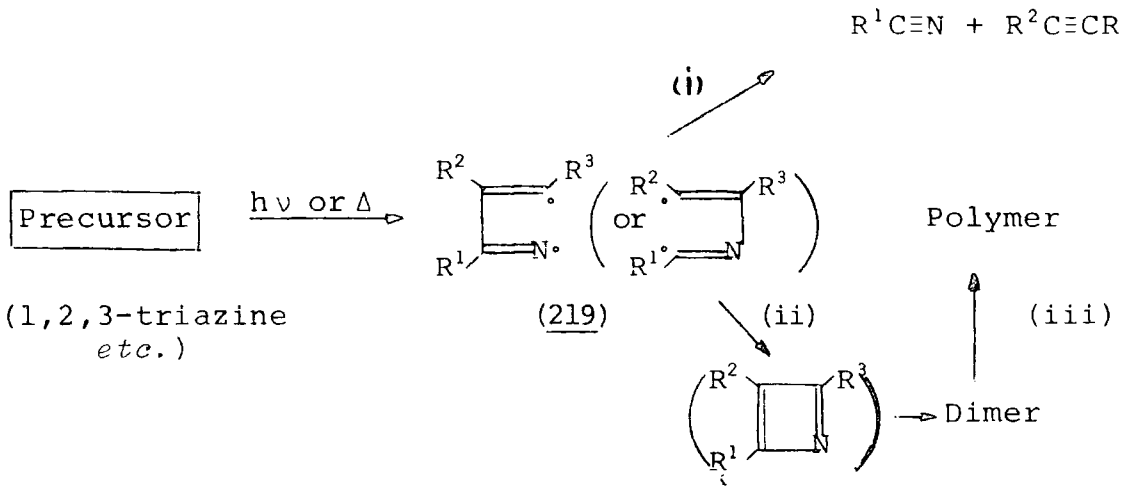


(R_f=CF(CF$_3$)$_2$)

(192)

the most stable azete is (80) because of π-electron donating groups at the 2- and 4-positions and electron-withdrawing group at the 3-position. The azete (181) may be the least stable. However, both azetes gave dimers, whereas azetes (175) and (192) with stability between them yielded polymer and fragmentation products, respectively, as summarized in Scheme 7.3. Three factors are taken into consideration which may destine the diradical intermediates (219), produced from appropriate percursors. (Clearly, 1,2,3-triazine system is one of them). With bulky substituents at the adjacent ring-carbons, the diradical (219) undergoes further fragmentation (R^1=R^2=R^3=CF(CF$_3$)$_2$,[11] N(CF$_3$)$_2$,[24] Aryl[20] *etc.*). However, without such steric repulsion, the intermediate (219) may form an azete, which could be stabilized by "push-pull" substituents (R^1=R^3=F, R^2=CF(CF$_3$)$_2$[15] : R_1=R_2=R_3-N(CH$_3$)$_2$[10]). In addition, it is probable that radical destabilizing groups facilitate ring-formation and dimerization (R^1=R^2=CF(CF$_3$)$_2$,R^3=F). There are some azetes with less bulky groups leading to frag-

Scheme 7.3



(i) Steric repulsion among substituents

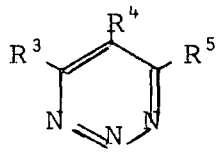
(ii) Push-pull stabilization for the cyclic intermediate or destabilization of substituents for the diradical

(iii) Small steric hindrance

---

mentation (R^1=R^2=CH_3, R^3=H[12]; R^1=R^2-H, R^3=CH_3[12] *etc.*) after formation of the cyclic structure. Polyaddition occurs between a dimer and an azete with small steric hindrance in a certain case (R^1=R^2=R^3=F).

Therefore it seems probable that the following azetes will be synthesized from 1,2,3-triazines and undergo dimerization and cycloadditions.



R^3, R^5 = F, CN, CF_3, R_f

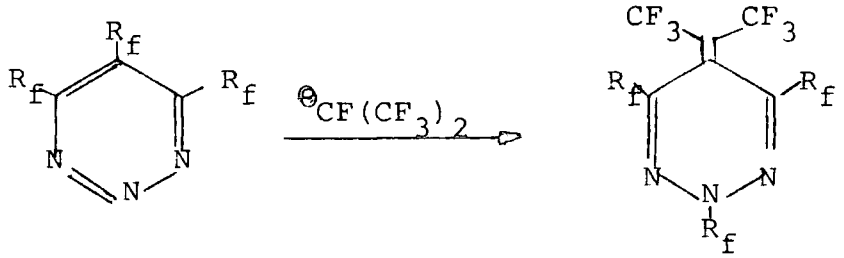
R^4 = H, F, CN, CF_3 (CH_3)

CHAPTER EIGHT

NUCLEOPHILIC REACTION

8.1 Introduction

Formation of the unusual product (166) has been shown to involve nucleophilic attack by perfluoroisopropyl anion on the nitrogen at the 2-position in perfluorotrisisopropyl-1,2,3-triazine (165). A Grignard reagent also has proved

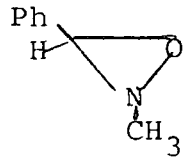
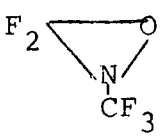
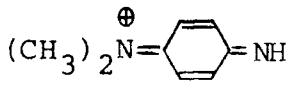
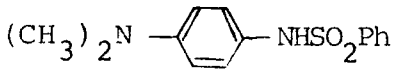
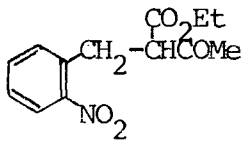
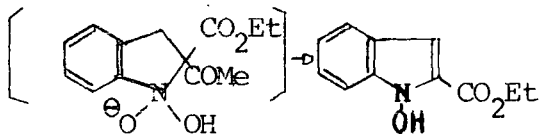
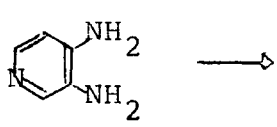
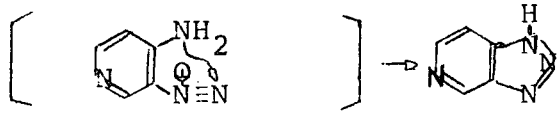
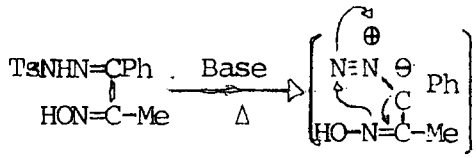
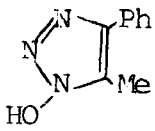
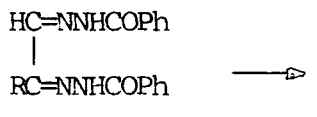
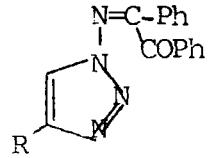
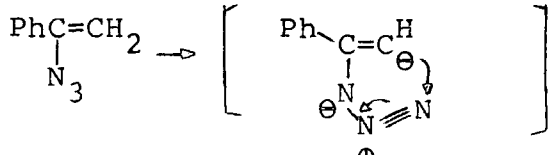
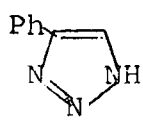
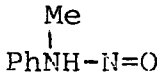


(165) (166)

to react with (165) in the same manner (see Chapter Five). However nucleophilic attack on nitrogen is rare since lone pair electrons on nitrogen usually attract electrophiles. No reaction has been reported towards ring-nitrogen not only in 1,2,3-triazine systems where adjacent nitrogens could increase its basicity and are susceptible to electrophilic attack (see Chapters One and Three), but also in heteroaromatic compounds. Some known examples that involve nucleophilic reaction on nitrogen may be summarized in Table 8.1, including dipolar cycloadditions.

Further attempts are discussed in this chapter to obtain products by nucleophilic reactions to the triazine (165), in

TABLE 8.1 Nucleophilic Attack on Nitrogen

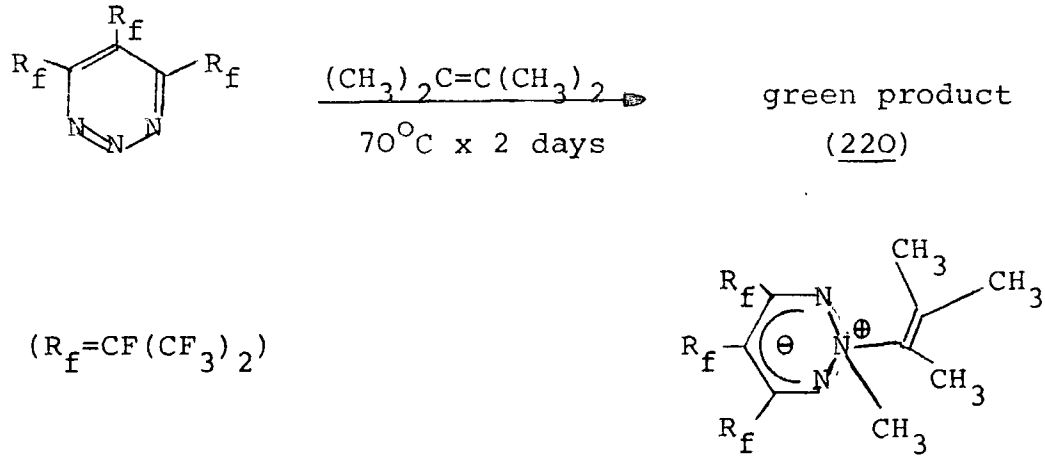
Reactant	Process	Product	Lit.
	Me_2NH	PhCHO + $Me_2N-\overset{H}{N}-Me$	216
	CH_3OH	$CF_3N(OCH_3)-COF$	217
	$^{\ominus}SO_2Ph$, $OH^{\ominus}$		218
	$OH^{\ominus}$		219
			220 221
	Base, Δ		222
			223
			224
CH_3CONH_2	$H_2\overset{\oplus}{O}-N=O$	$[CH_3\overset{\oplus}{C}(NH_2)-N=O] \rightarrow CH_3CO_2H$	225
	$S=C(NH_2)_2$	PhNHMe + $ON-\overset{\oplus}{S}C(NH_2)_2$	226
PhN_3	$^{\ominus}CN$	Ph-NH-N=N-CN	227

order to over-view the feature of the system, which includes reaction with alkenes as soft bases.

8.2 Substituted Ethylenes

(A) 2,3-Dimethylbut-2-ene

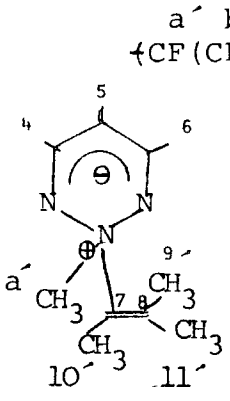
Thermal reaction of (165) with 2,3-dimethylbut-2-ene was carried out to give a green coloured 1:1 adduct in 89% yield. The structure of the green liquid (220) was assigned



as an intramolecular Zwitterionic species (an ylid). This follows from the spectroscopic data as shown in Table 8.2, by the comparison of those of (165) in Table 8.3. There is an absence of fine structures in the ^{19}F n.m.r. spectrum of (220), which are observed in (165). This is not fully understood but the difference indicates a change in stereochemistry, involving three carbon atoms of the ring, to which perfluoroalkyl groups attached. More important, the significant upfield shift of the tertiary fluorine on the perfluoroisopropyl group at the 5-position (23 p.p.m.) indicates the increased electron density[233,234] on the 5-carbon. The electron density is more efficiently reflected in the ^{13}C chemical shifts of

TABLE 8.2 Spectroscopic data for (220)

^{19}F n.m.r. spectrum (neat; ext.ref. $CFCl_3$)

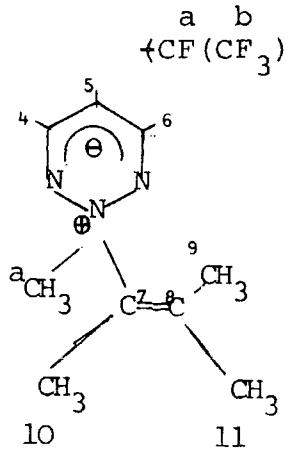


Shift (ppm)	Structure	Intensity	Assignment
73.7	S	6	4b´ or 6b´
75.9	S	6	5b
78.0	S	6	6b´ or 4b´
177.9	S	1	5a´
122.0	S	2	4a´ and 6a´

^{1}H n.m.r. spectrum (neat; ext.ref. TMS)

Shift (ppm)	Structure	Intensity	Assignment
1.47	S	9	9´,10´,11´
4.82	S	3	2a´

^{13}C n.m.r. spectrum (neat; ext.ref. TMS)



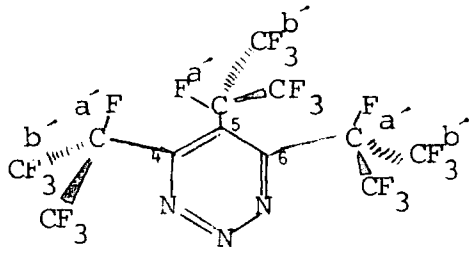
Shift (ppm)	Structure	Intensity	Assignment
152.3	S	1	8
125.8	Q(J=292.9Hz) of M	6	4b,5b,6b
123.6	D(J=37Hz)	>1	4 and 6
118.1	S	1	7
95.7-98.4	M	(≥3)	4a,5a,6a
78.1	S	1	2a
37.2	D(J=25Hz)	1	5
30.4	S	>2	10,11
23.2	S	1	9

I.R. Spectrum

1560 cm^{-1}, 1650 cm^{-1}

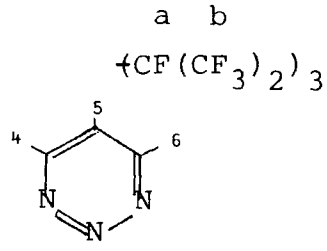
TABLE 8.3 Spectroscopic data for (165)

^{19}F n.m.r. spectrum (neat; ext.ref. $CFCl_3$)



Shift (ppm)	Structure	Intensity	Assignment
74.2	D(J=39Hz)	6	5b´
74.5	D(J=17.5)of D(J=3.9)	6	4b´
75.3	S	6	6b´
154.7	D(J=117)of Sept(J=40)	1	5a´
180.3	D(J=117)of Sept(J=3.9)	1	4a´
184.6	Sept(J=39)	1	6a´

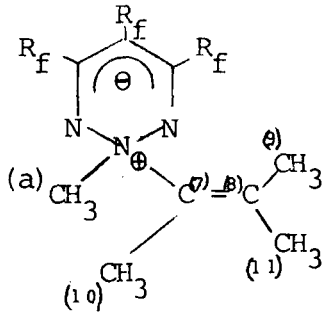
^{13}C n.m.r. spectrum ($(CD_3)_2C=O$; int.ref. TMS)



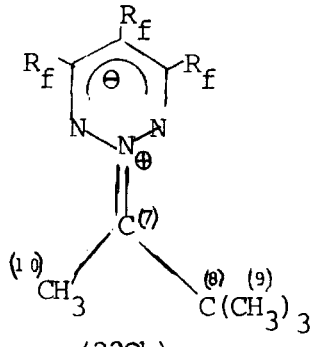
Shift (ppm)	Structure	Assignment
148.1	D(J=27.9Hz)	6
145.5	D(J=29.3)of D(J=2.8)	4
119.0	Q(J=288.3) of D(J=27.8)	4b,6b
118.9	Q(J=289.2) of D(J=26.5)	5b
118.0	D(J=30.3)	5
93.8	D(J=175.4) of Sept(J=36.5)	5a
92.8	D(J=217.0 of Sept(J=34.0)	4a,6a

the ring carbons, which are easily revealed by a coupling of 20-40 Hz between ring carbons and the tertiary fluorine of an attached perfluoroisopropyl group.[228] The chemical shift of the 5-carbon is moved to up-field (80.8 p.p.m.) from the value of the triazine (165) and the effects on the 4- and 6-carbons are the same direction, *i.e.* up-field shift, though the magnitude is much smaller (av. 23.3 p.p.m.) which is consistent with the charge being greater on the positions ortho and para to the site of attack. Appropriate models for these observations are probably the products of addition to phospha- and arsino-benzenes (Table 8.4), where all sites are moved up-field in the product, whereas in some Meisenheimer σ-complexes, and pyridine N-oxide the sites meta to the position of nucleophilic attack are moved to downfield. The assignment of signals corresponding to perfluoroisopropyl groups is obvious because of large C-F coupling (200-300 Hz) which appears in the region close to those observed in the starting triazine (165).

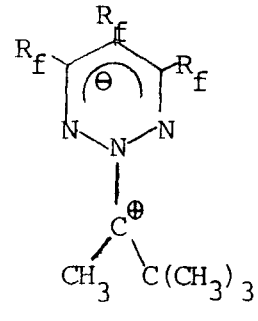
The ^{1}H n.m.r. spectrum shows that three of four methyl groups are equivalent and that the remaining group is attached to a considerably electron-deficient site, *i.e.* either carbocation[235] or qua-ternary ammonium salt[244] (Table 8.5). From these observations, three possible structures could be attributable to (220) *i.e.* (220a) - (220c).



(220a)



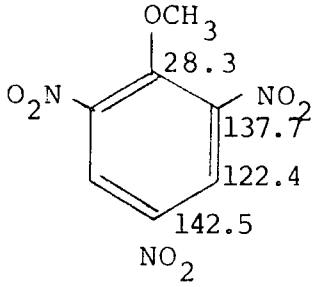
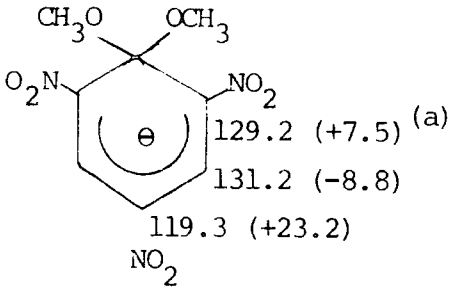
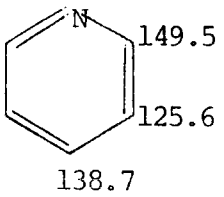
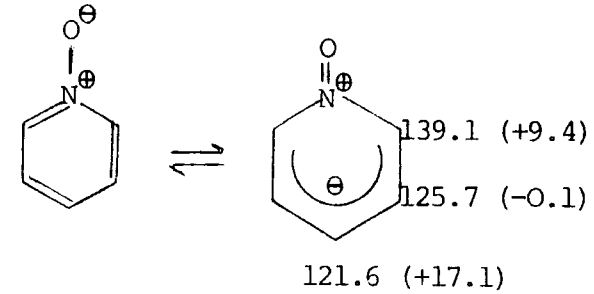
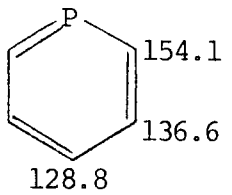
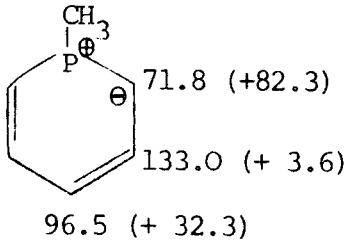
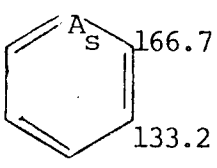
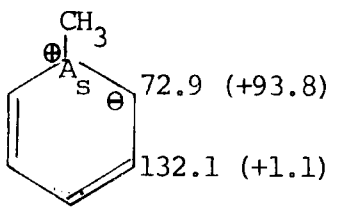
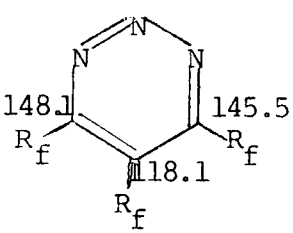
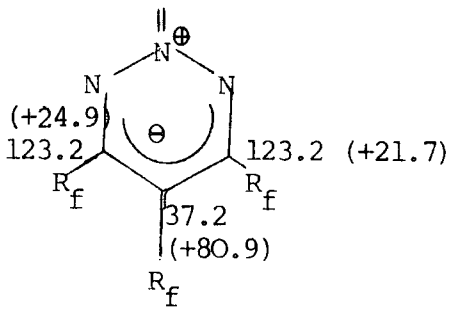
(220b)



(220c)

(R_f=$CF(CF_3)_2$)

TABLE 8.4 ^{13}C-Chemical Shifts of Cyclic Anions

Precursor	Anion	Lit.
	 (a)	229
		232
		230 231
		230
		

(a) The values in parentheses represent the difference of the chemical shifts between precursors and anions. Positive sign indicates up-field shift.

TABLE 8.5 Chemical Shifts (^{1}H and ^{13}C n.m.r.) of Model Compounds

235,238

$(CH_3)_3C^{\oplus}$

4.20[a]

51.5[b] 320.6

236, 240

$(CH_3)_2\overset{\oplus}{N}=CH_2$

3.41

49.7 168

235,238

$(CH_3)_2\overset{\oplus}{C}-C(CH_3)_3$

2.86 2.86

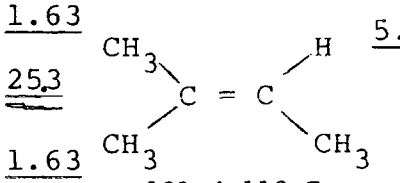
33.6 197.3 33.6

241

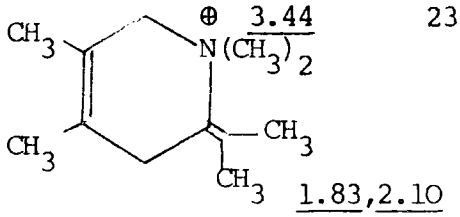
$(CH_3)_2C=\overset{\oplus}{N}(\text{pyrrolidine})_2$

2.52

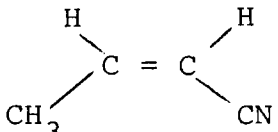
243,(c)



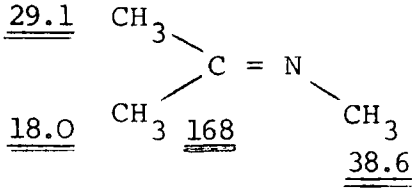
237



244



242



239,(c)

$(CH_3)_3CCH=CH_2$

1.0

29.8 35.8 149.4 109.4

1.96 4.4 1.80 (c)

$(CH_3)_2\underset{Br}{C} - \underset{Br}{CHCH_3}$

1.1 (c)

$(CH_3)_3C\underset{Br}{CH} - \underset{Br}{CH_2}$

(a) - ^{1}H n.m.r. chemical shift

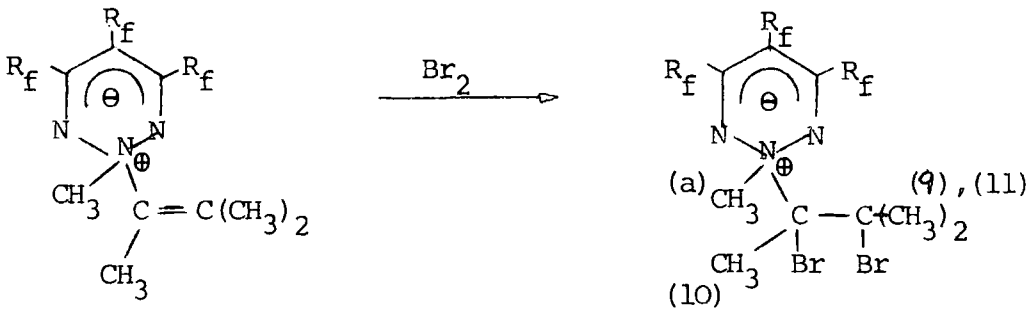
(b) = ^{13}C n.m.r. chemical shift

(c) measured values.

However, the ^{13}C n.m.r. spectrum does not show any signals in such downfield (195-400 p.p.m.) corresponding to carbocations, which rules out the structure (220c).

Distinction of the enamonium salt (220a) from the iminium salt (220b) was established as follows. The ^{1}H n.m.r. spectrum is not decisive but more consistent with (220a) by the comparison with models, *i.e.*, both shifts are too low field for (220b). In the ^{13}C n.m.r. spectrum, the signals at 23.2 and 30.4 p.p.m., *i.e.*, the region for saturated carbons, are attributable to either C-9, -10 and -11 in (220a) or C-8 and -9 in (220b) and the signal (152 p.p.m.) in the lowest field to unsaturated carbons in both structures, *i.e.*, C-8 in (220a) or C-7 in (220b). However, the remaining two signals (118.1 and 78.1 p.p.m.) can be explained only by the structure (220a) since C-10 in (220b) cannot accommodate them. Also structure (220b) would require assignment of signals at 123.6 and 118.1 (Table 8.2) in the ^{13}C n.m.r. spectrum to C-4 and C-6, which is, of course, unacceptable.

In order to confirm the identification, bromination of (220) was carried out yielding an adduct (221), which clearly

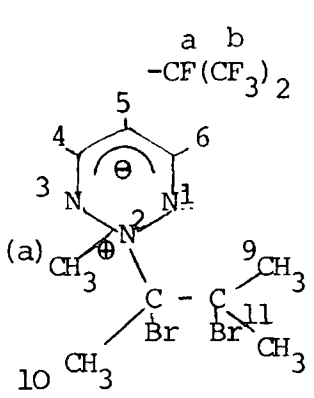


(220) (221)

indicates the structure (220a). The ^{1}H n.m.r. spectrum of (221) in Table 8.6, shows that the C-10 is no longer equivalent to the C-9 and -11, all of which shifted to the low field, *i.e.* the same observation as in the case of bromination of 2-methylbut-2-ene (Table 8.5). Furthermore the shift of the methyl group attached to the qua-ternnary ammonium salt was moved up-field to the region, characteristic of dimethyl-derivatives (Table 8.5). In contrast the ^{19}F chemical shifts remained unchanged. These observations were accompanied by the disappearance of the absorption at 1660 cm^{-1} in the i.r. spectrum which corresponds to carbon-carbon double bonds in substituted ethylenes.[244]

TABLE 8.6 Spectroscopic data for (222)

^{19}F n.m.r. spectrum (solvent ($CDCl_3$; ext. ref. $CFCl_3$)



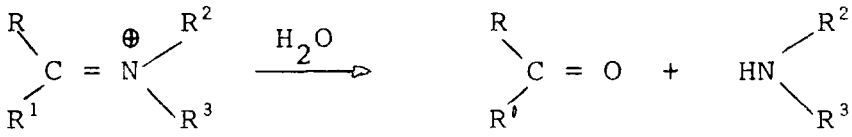
Shift (ppm)	Structure	Intensity	Assignment
73.4	S	6	4b or 6b
75.6	D(J=5.6)	6	5b
77.2	D(J=5.6)	6	6b or 4b
177.7	S	1	5c
181.0	S	2	4c, 6a

^{1}H n.m.r. spectrum (solvent $CDCl_3$; int. ref. TMS)

Shift (ppm)	Structure	Intensity	Assignment
3.90	S	3	2a
1.80	S	6	9,11
1.70	S	3	10

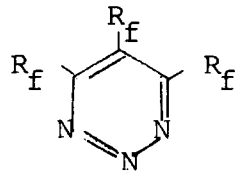
I.R. Spectrum 1560 cm^{-1}

Furthermore, attempted hydrolysis and methanolysis of (220) failed, which again confirms the structure (220a), since iminium salts are highly moisture sensitive and give ketones and amines.[247(b)]



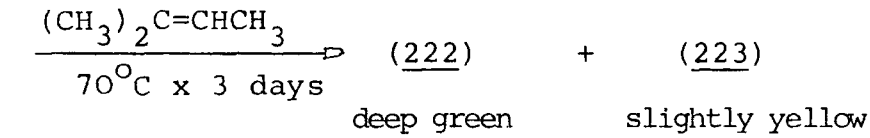
(B) 2-Methylbut-2-ene

2-Methylbut-2-ene reacted with the triazine (165) to yield two products, one of which is a deep green liquid (222) and has been assigned an analogous structure to (220), since this major product (222) shows almost identical spectroscopic

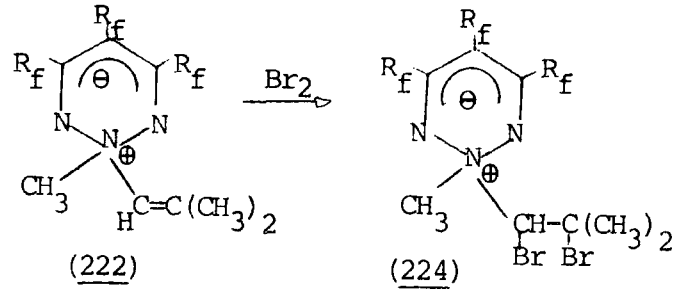


(165)

$(R_f=CF(CF_3)_2)$



(222) deep green 56% + (223) slightly yellow 33%



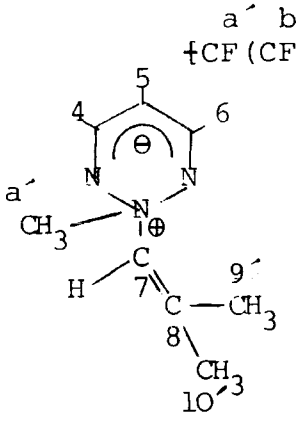
(222) (224)

data to (220) (Table 8.7) and (222) was also confirmed by formation of a bromine adduct (224). The minor product (223), a slightly yellow liquid, has the same molecular weight as (222) but shows completely different spectra (Table 8.8).

The ^1H n.m.r. spectrum clearly indicates formation of a vinylic system which has a methyl and a proton at the geminal

TABLE 8.7 Spectroscopic data for (222)

^{19}F n.m.r. spectrum (neat; ext.ref. $CFCl_3$)

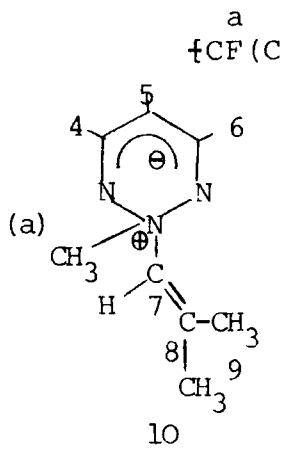


Shift (ppm)	Structure	Intensity	Assignment
73.4	S	6	4b′ or 6b′
75.7	S	6	5b′
77.9	S	6	4b′ or 6b′
177.6	S	1	5a′
181.5	S	2	4a′ and 6a

^{1}H n.m.r. spectrum (neat; ext.ref. TMS)

Shift (ppm)	Structure	Intensity	Assignment
4.80	S(broad)	3	2a′
4.60	M(shoulder)	1	7′
1.57	S(broad)	6	9′, 10′

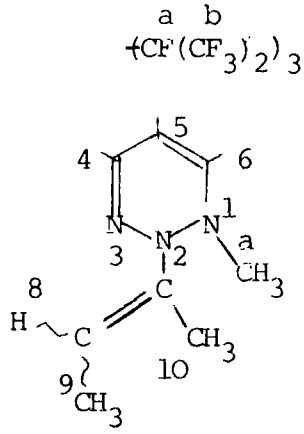
^{13}C n.m.r. spectrum (neat; ext. ref. TMS)



Shift (ppm)	Structure	Assignment
148.0	S	8
125.0	Q(J=283.4Hz) of M	4b,5b,6b
123.2	D(J=37.2Hz)	4 and 6
119.7	S	7
97.4-94.0	M	4a,5a,6a
76.2	S	2a
36.6	D(J=25Hz)	5
23.1	S	10
21.4	S	9

TABLE 8.8 Spectroscopic data for (223)

^{19}F n.m.r. spectrum (solvent $CDCl_3$; ext.ref. $CFCl_3$)



Shift (ppm)	Structure	Intensity	Assignment
71	S	3)	
		)	4b,5b,6b
73-74	M	15)	
160.0	D(J=160Hz)	1	5a
174.4	Q(orT)(J=46Hz)	1	6a
174.8	D(J=160Hz)	1	4a

^{1}H n.m.r. spectrum (solvent $CDCl_3$; ext.ref. TMS)

0.93	D(J=5Hz)	3	9
1.73	S	3	10
4.10 (4.11) (4.24) (a)	M(J=5Hz)	1	8
4.83	S	3	1a

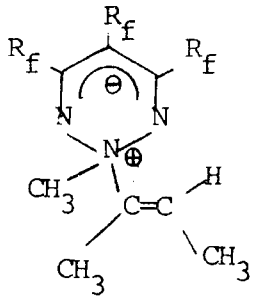
I.R.spectrum 1665 cm^{-1}

(a) Calculated values; 4.11 and 4.24 for cis-and trans-butenyl groups respectively.

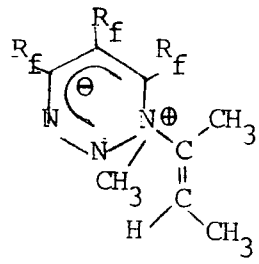
---

position because of the coupling with typical J-value (5Hz).

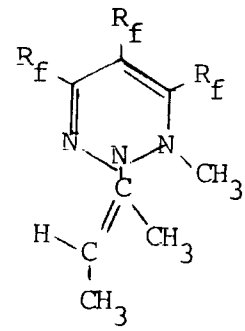
It also shows a methyl group at such low field (4.83 ppm) as to indicate attachment to a strongly electron-withdrawing site, but the ^{19}F chemical shifts and fine structures are inconsistent with an internal salt (223a). The complexity of the fine structure of the tertiary fluorine on the perfluoroisopropyl group at the 6-position suggests that a substituent has been introduced on the adjacent nitrogen and hence the possible structures (223b) - (223d). However, the structure (223b) is not consistent with the charge distribution on the



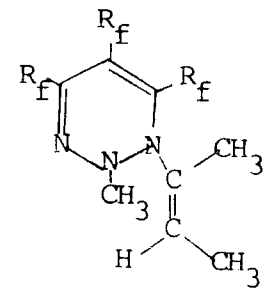
(223a)



(223b)

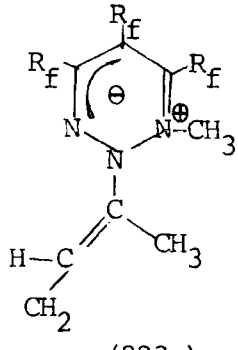


(223c)

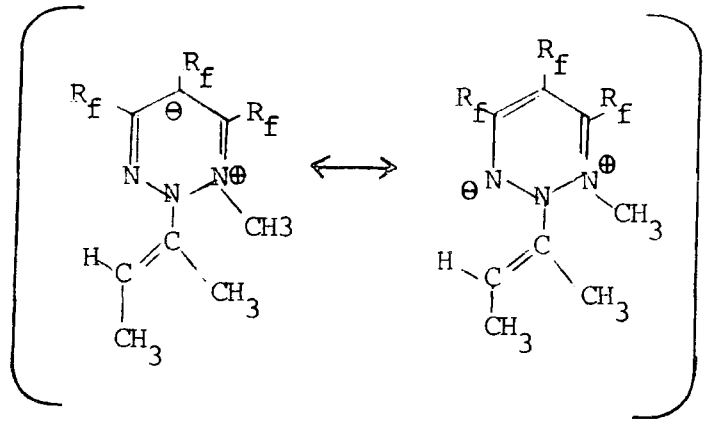


(223d)

ring which is reflected in the down- or up-field shifts of the tertiary fluorines from those observed in the starting triazine (165). Thus the spectroscopic data is accounted for only by the structure (223c)or more appropriate written as resonance forms (223e) as structure (223d) would lead to highest charge density at the 4- and 6-positions which is not in accord with ^{19}F n.m.r. data. It is probable that



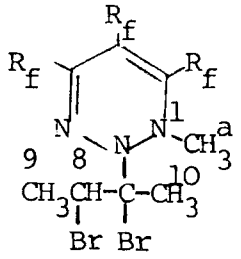
(223e)



the strong electron-withdrawing character of the perfluoroisopropyl groups leaves the nitrogen at the 1-position electron-deficient. Addition of bromine in a solution of (223) caused considerable shifts of the signals in the ^{1}H n.m.r. spectrum

(Table 8.9) whereas the ^{19}F n.m.r. spectrum remained unchanged, which was accompanied by disappearance of the absorption at 1665 cm^{-1} in the i.r. spectrum as in the cases of (220) and (222), confirming the structure.

TABLE 8.9 ^{1}H n.m.r. spectrum of bromine adduct (225)



(225)

Shift (ppm)	Structure	Intensity	Assignment
10.3	broad	3	10
1.93	D broad (J=9.3Hz)	3	9
3.8	broad	3	1a
5.7	broad	1	8

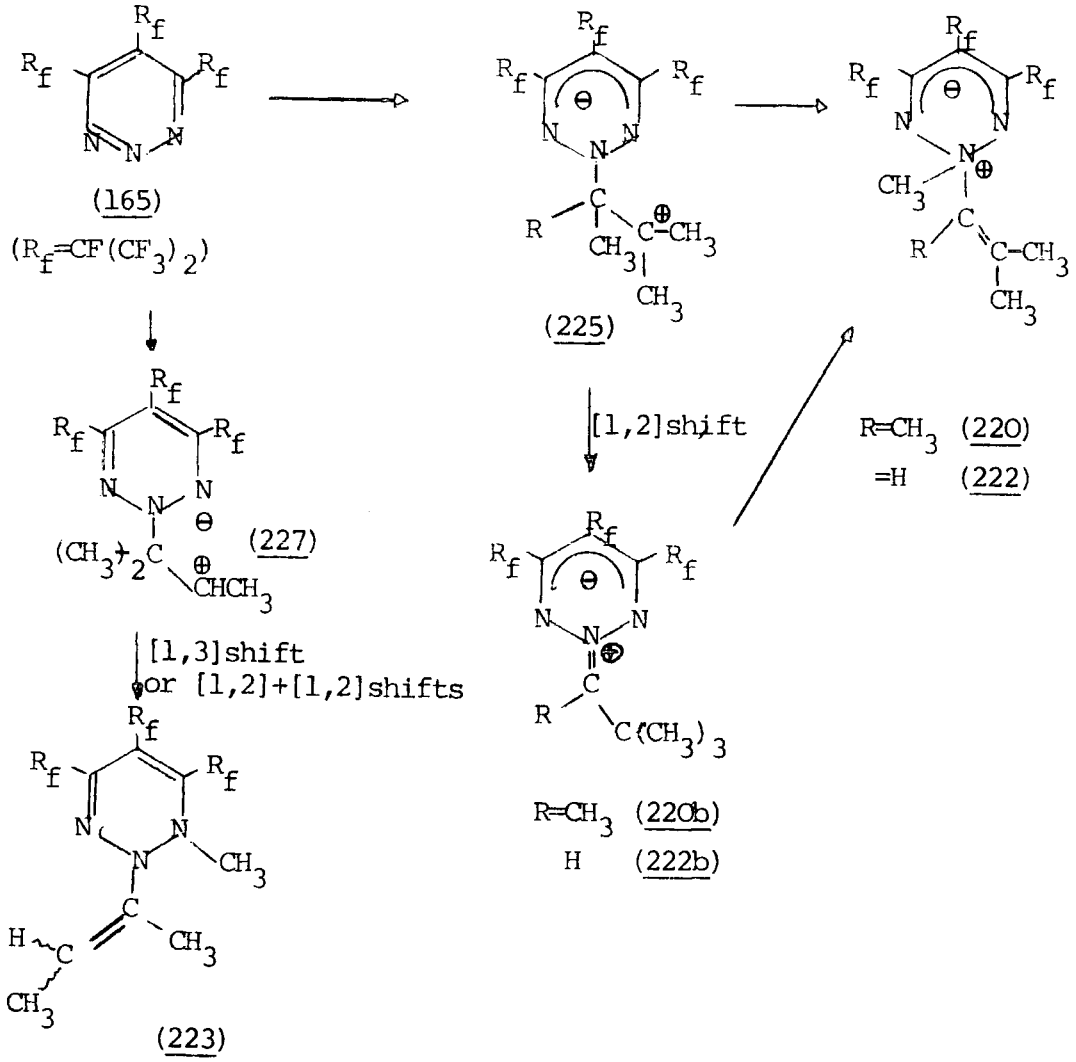
(C) Attempted Reaction with 3,3-Dimethylpropene

Addition reaction of 3,3-dimethylpropene with the triazine (165) was attempted at 70°C for 2 weeks and 100°C for 3 days without success, to recover the starting materials.

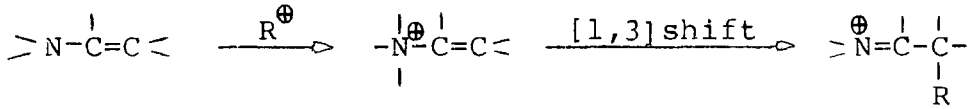
(D) Mechanism of Adducts Formation

The formation of the intramolecular enamonium salts (220) and (222), probably also involves nucleophilic attack of the alkenes on the nitrogen at the 2-position of the triazine (165). Then [1,2] methyl shift to the nitrogen follows, forming a double bond as shown in Scheme 8.1. It may also be possible to predict the intermediacy of the iminium salts (220b) and (222b), which could be formed by [1,2],methyl shift to the carbocation in the primary adduct (225), since [1,2] shifts are the most common type of skeletal rearrangement involving carbo-cations.[246] Iminium salts are formed from enamine, *via* enamonium salts[247(b)] as kinetic products and therefore, we

Scheme 8.1 Reaction with $RC(CH_3)=C(CH_3)_2$

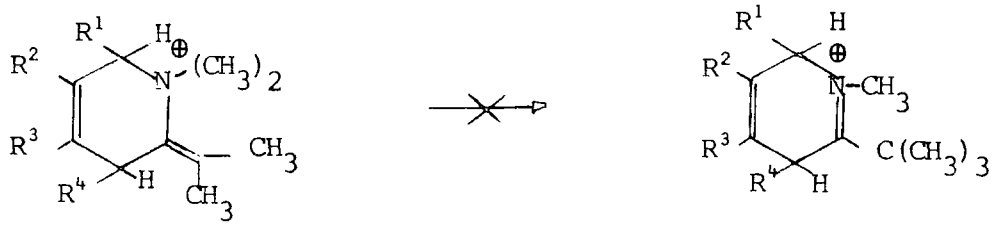


would expect the process *via* intermediates (220b) and (222b) to be the most likely. In spite of this, the products (220)



and (222) are remarkably stable up to 200°C without rearrangement to the corresponding iminium salts. It is probable that the nitrogens at the adjacent position stabilize the enamonium form and the stereochemistry of the system does not favour the shift of the methyl group.

Enamonium salts (228), synthesized by addition reaction of a ketenium salt, are not converted iminium salts,[237,247(c)]



(228)

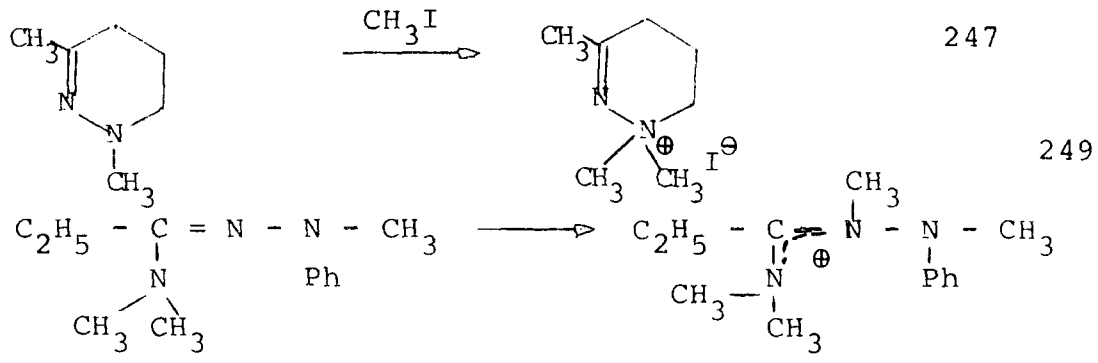
(a) $R^1 = R^4 = H$, $R^2 = R^3 = CH_3$

(b) $R^2 = R^3 = H$, R^1, $R^4 = -CH_2-$

(c) $R^2 = R^3 = H$, R^1, $R^4 = -(CH_2)_2$

This is another example where the enamonium salts (228) are more stable than the iminium salts.

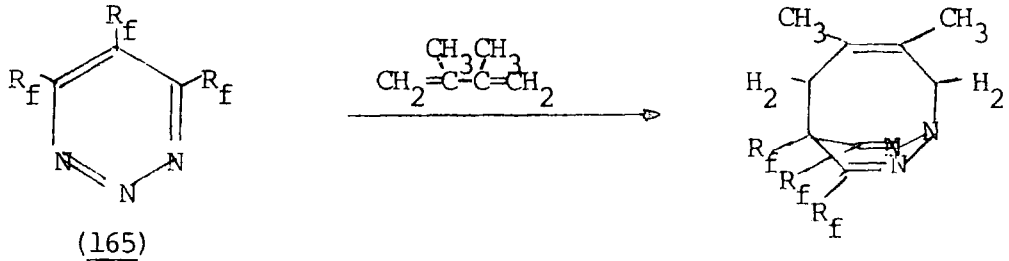
Formation of the by-product (223) also probably proceeds in the same manner *via* the intermediate (227), followed by [1,3] methyl shift to the nitrogen at the 1-position or alternatively, *via* enamonium salt (223a). Qua-ternarization of hydrazones usually occurs on the sp^3 nitrogen because of higher nucleophilicty.[248] However, some exceptions exist if alkylation on the sp^2 nitrogen leads to a salt with delocalization of the positive charge.[249,247(a)] It may be this factor that promotes the methyl shift to the nitrogen at the 1-position, although the driving force to give different species (222) and (223) is not fully understood, except that it seems to relate to the terminal substituents.



Relative reactivity of alkenes was in the order of $(CH_3)_2C=C(CH_3)_2$ > $(CH_3)_2C=CHCH_3$ >> $CH_2=CH-C(CH_3)_3$, which is consistent with those observed in halogenation reactions.[245]

8.3 2,3-Dimethylbuta-1,3-diene

Thermal reaction of perfluorotrisisopropyl-1,2,3-triazine (165) with 2,3-dimethylbuta-1,3-diene was carried out at 70°C, to afford a 1:1 adduct (229) in 70% yield. The structure of



(165)

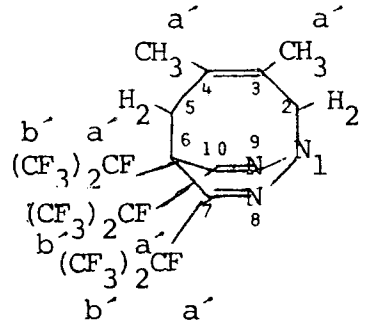
(R_f=$CF(CF_3)_2$)

(229)

brilliant yellow solid was determined on the basis of spectroscopic data (Table 8.10). In the ^{19}F n.m.r. spectrum, the equivalent perfluoroisopropyl groups at the 7- and 10-positions appear slightly different because of crowdiness of the substituents as seen in other related compounds (Chapter Five). However, the symmetry of the molecule is revealed in the ^{13}C n.m.r. spectrum, which shows two equivalent perfluoroisopropyl groups

TABLE 8.10 Spectroscopic data for (229)

^{19}F n.m.r. spectrum (Solvent $CDCl_3$; ext.ref. $CFCl_3$)

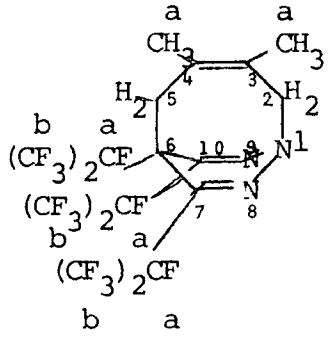


Shift (ppm)	Structure	Intensity	Assignment
73.5	S	6	7b´ or 10b´
75.8	S	6	10b´ or 7b´
73-76	Broad	6	6b´
152.3	Sept.Broad	1	6a´
181.0	S broad	2	7a´ and 10a´

^{1}H n.m.r. spectrum (solvent $CDCl_3$; int. ref. TMS)

Shift (ppm)	Structure	Intensity	Assignment
4.82	S	2	5
4.28	S	2	2
1.8	S	6	3a´, 4a´

^{13}C n.m.r. spectrum (solvent $CFCl_3$; int.ref. TMS)

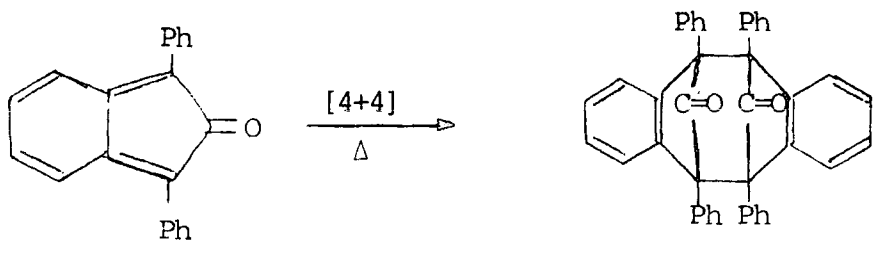


Shift (ppm)	Structure	Assignment
155.9	M	7, 10
124.8	S	3
124.1	S	4
121.1	D(J=29.2Hz) of Q(J=288.8Hz)	6b
119.9	D(J=27.3Hz) of Q(J=287.5Hz)	7b,10b
94.7	D(J=218.2Hz) of Sept(J=35Hz)	6a
93.4	D(J=54.1Hz)	6
91.4	D(J=245.0Hz) of Sept(J=33.8Hz)	7a,10a
83.7	S	2
74.3	S	5
11.1	S	3a
10.8	S	4a

I.r. spectrum 1570 cm^{-1} (m), 1440 cm^{-1} (m)

and unsaturated carbons. Additional sites of unsaturation are also observed at 124.8 and 124.1 p.p.m., which are attributable to the butene segment.

The bicyclic compound (229) is formally a thermal [4+4] cycloaddition product which is a symmetry-forbidden reaction.[191,211] [4+4] Cycloaddition is quite rare even photochemically[250] and only one thermal reaction has been reported, so far, which is dimerization of an inden-2-one.[251]



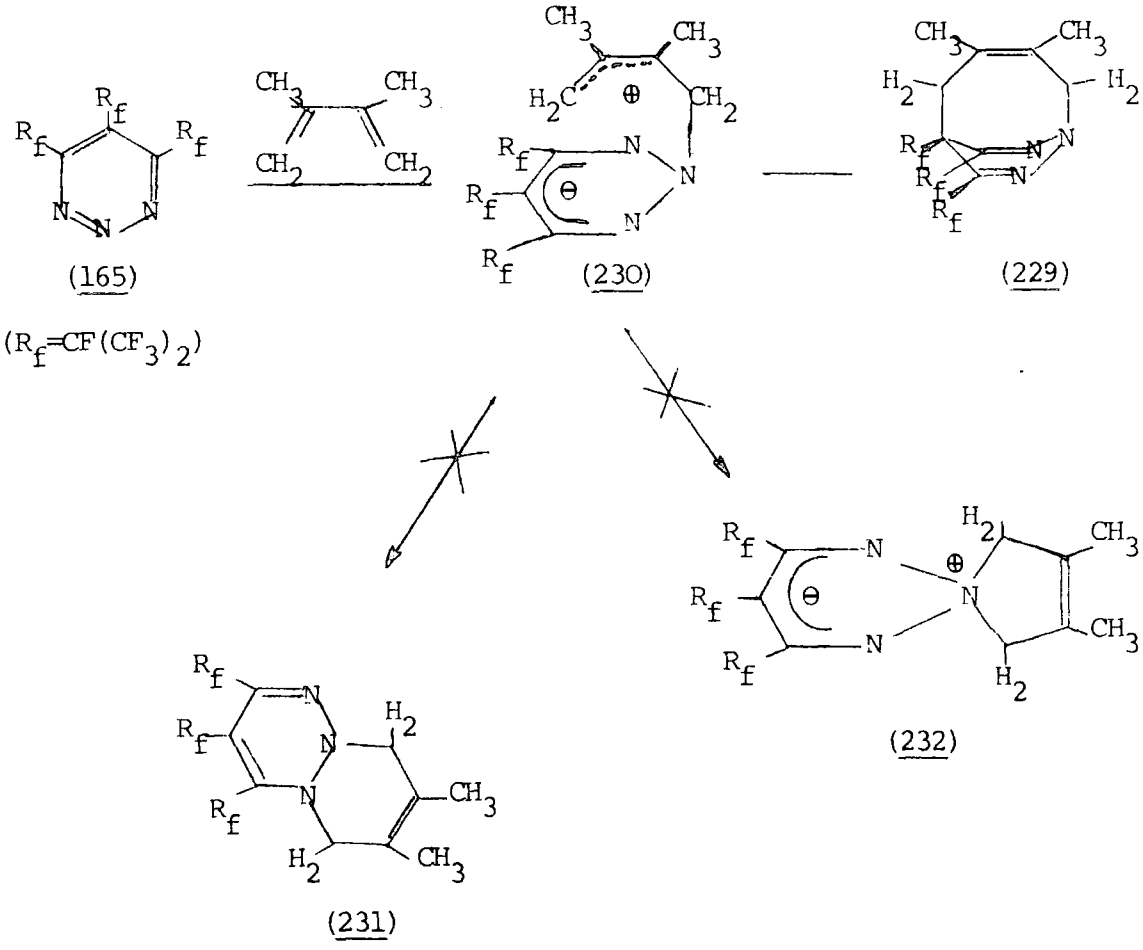
251

The formation of (229) is probably a non-concerted process which involves ionic species (230) in Scheme 8.2, by the analogy with the reaction of substituted ethylenes described in 8.2.

It is likely that stabilizing effects of methylene groups on the cation is not large enough to form the Zwitterionic species (232), compared with methyl- and vinyl-groups in (220) and (222). Furthermore the attractive interaction between charges in the proposed intermediate (230) and the less sterically-hindered terminal methylene group probably favour the addition reaction to the 5-carbon as an anionic centre, over formation of (231).

Attempted pyrolysis of (229) at 200°C resulted in formation of black polymer, without further investigation.

Scheme 8.2



(165) (R_f=$CF(CF_3)_2$)

(230)

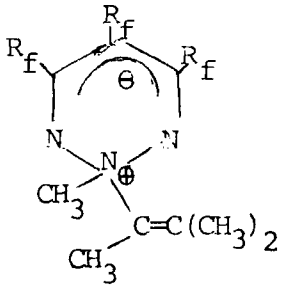
(229)

(232)

(231)

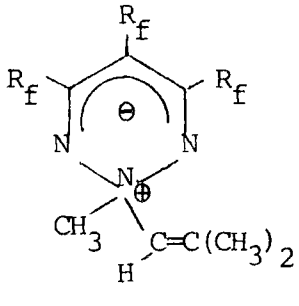
8.4 Properties of Adducts

The colour of the adducts of (165) with alkenes suggest that they form intramolecular charge transfer complexes. In fact the u.v. spectrum of (229) exhibit an additional absorption



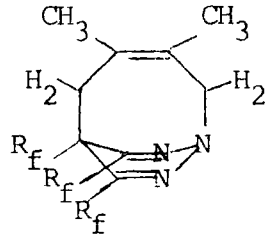
(220)

green liquid



(222)

deep green liquid

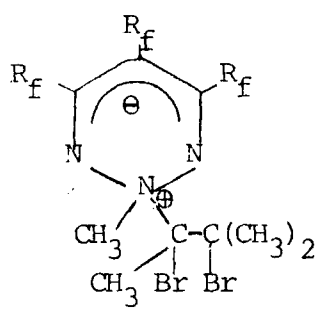


(229)

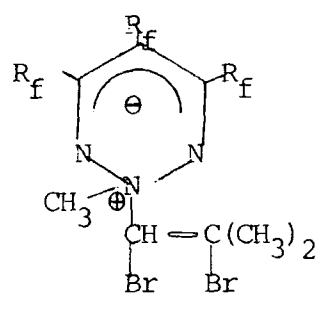
brilliant yellow crystals

TABLE 8.11 U.V. Spectra of Adducts

Adduct	λ_{max}, nm (ε, ℓ mole^{-1} cm^{-1})	
	Solvent: AcCN	Cyclohexane
(222)	248 (4370)	244 (5960)
	302 (4550)	298 (5200)
	392 (160)	404 (300)
(220)	213 (2700)	218 (3600)
	248 (5170)	247 (8200)
	294 (4090)	292 (6200)
	-	398 (30)
(229)	195.3 (10100)	199.8 (6620)
	264.7 (5570)	263.8 (5520)
	340.5 (3400)	343 (3640)
(221)	251.2 (10300)	-
	296.2 (6730)	-
(224)	249.2 (10400)	-
	283.0 (6970)	-
	367 (790)	-

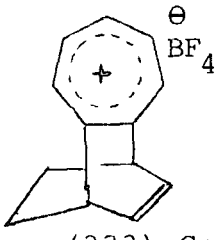


(221)

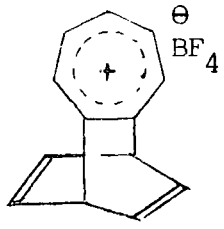


(224)

at 340nm (CH_3CN) which undergoes bathchromic shift in a less polar solvent (cyclohexane) *i.e.*, typical phenomena observed in charge-transfer complexes[252,253] (Table 8.11). The wavelength is analogous to those found recently in intramolecular charge-transfer complexes (233)[254] and (234).[255] However, the



(233) Colourless[254]



(234) greenish yellow[255]

λ_{max} (log ε)	230.7	(4.65)	230.2	(4.69)
	276	(3.77)	270.7	(4.04)
	325	(3.15)	334	(3.56)
			374	(sh)

corresponding absorptions (*ca.* 300nm) in (220) and (222) shows hypsochromic shifts and more important, large hyperchromic effects of the less polar solvent was observed, suggesting that the interactions between the zwitterions have predominant effects on the charge-transfer process. The process may include those through σ-bond[256] or lone-pair electrons on nitrogens and π-electrons on the vinyl substituents. Indeed, the greenish colour of (220) and (222) changed to a slightly yellow after addition of bromine, which coincides with large hypsochromic shifts in (222).

8.5 Other Attempts

(A) Hard bases

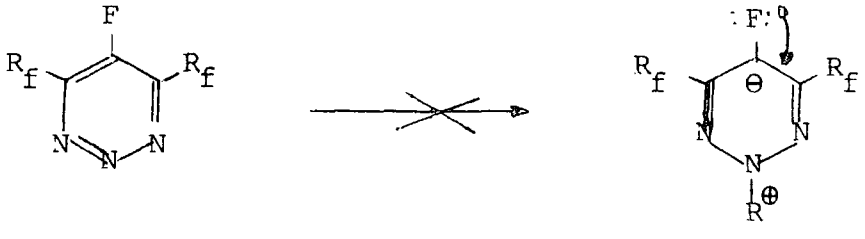
Reactions of the triazine (165) with methoxide and triethylamine were attempted without success, forming red tar without further investigation.

(B) Cycloaddition with dienophile and dipoles

Cycloaddition reactions of the triazine (165) with dimethyl acetylenedicarboxylate, phenylazide, and diazomethane were attempted at 70°C, room temperature, and room temperature respectively without success. These results again confirm the electron deficient character of the triazine ring: since these are usually three of the most reactive reagents towards electron rich alkenes and heterocycles.[257]

(C) Perfluoro-4,6-bisisopropyl-1,2,3-triazine with alkenes

Reactions of perfluoro-4,6-bisisopropyl-1,2,3-triazine (165) with 2-methylbut-2-ene and 2,3-dimethylbuta-1,3-diene were attempted without success. It is probable that the fluorine at the 5-position suppressed the formation of the intermediate because of non-bonding repulsion of lone-pair electrons on fluorine against anion as in the case of nucleophilic reactions of polyfluoroaromatics.[110]



8.6 Conclusion

It has been shown in the chapters that novel nucleophilic reactions of bases occur on the ring-nitrogen in perfluoro-trisisopropyl-1,2,3-triazine (165). The reactions include highly novel thermal [4+4] cycloaddition and formation of intramolecular charge-transfer complexes, featuring the triazine system.

In conclusion this evidence clearly shows the versatility of fluoro-compounds in synthetic chemistry.

EXPERIMENTAL

INSTRUMENTATION

Infrared spectra were recorded on a Perkin-Elmer 457 Gra-ting Infrared Spectrophotometer. Solid samples were recorded as KBr discs, liquid or low melting point solids as contact films between KBr plates and gaseous or low boiling point liquids in a cylindrical cell with KBr windows.

Proton and fluorine n.m.r. spectra were recorded on a Varian A56/60D spectrometer operating at 60 and 56.4 MHz respectively at the ambient probe temperature ($40^{o}C$), and on a Brüker HK90 with Fourier Transform facility at elevated temperatures. Chemical shifts are quoted in p.p.m. relative to TMS and $CFCl_3$. Carbon (^{13}C) and Nitrogen (^{15}N) spectra were recorded on a Brüker WH-360 operating at 90.6 and 36.5 MHz respectively. Chemical shifts are quoted in p.p.m. relative to TMS and $MeNO_2$.

Ultra violet spectra were recorded on a Pye-Unicam SP8-100 Ultraviolet Spectrometer, using acetonitrile or cyclohexane as the solvents.

Mass spectra were recorded on an A.E.I. M.S.-9 Spectrometer or on a V.G. Micromass 12B Spectrometer fitted with a Pye 104 Gas Chromatograph.

Gas liquid chromatographic analyses were carried out on a Varian Aerograph Model 920 or Pye 104 Gas Chromatograph using columns packed with 20% diisodecylphthalate on chromosorb P (Column A) or 20% Krytox (perfluoropolyoxypropylene) on chromosorb P (Column K). Preparative scale gas liquid chromatography was performed on a Varian Aerograph Model 920 using Columns A and K.

Fractional distillations of product mixtures were carried out using Fisher-Spaltrohr MMM202 system.

Carbon, hydrogen and nitrogen analyses were obtained using a Perkin-Elmer 240 Elemental Analyzer. Analyses for halogens were performed as described in the literature.[258]

Boiling points and melting points were determined at atmospheric pressure and are uncorrected. Boiling points were measured by the Siwoloboff method.

Reagents

Trichloroethylene and sodium trichloroacetate were obtained from the Aldrich Chemical Co. Ltd., Trimethylsilyl azide was prepared from trimethylsilylchloride and sodium azide.[104] Perfluoropropene was supplied by Asahi Glass Co. Ltd. (JAPAN). Other perfluoroalkenes used were purchased from Peninsular Chemical Research Inc. Diazomethane,[259] phenylmagnesiumbromide[260] and phenylazide[261] were prepared before use.

Tetrafluoropyridazine[264] was prepared by technical staff and stored over K F.

Caesium and potassium fluorides were dried by heating at 180°C under high vacuum for several days and powdered in a glove bag filled with dry nitrogen before reheating under vacuum and stored under a dry nitrogen atmosphere.

Sulpholane and acetonitrile were purified by fractional vacuum distillation. The middle fractions were collected over dried molecular sieve (Type 4A) and stored under an atmosphere of dry nitrogen.

Tetraglyme (supplied by I.C.I.) was purified by stirring with sodium metal at 95^{o}C for 3 hrs., followed by fractional distillation under vacuum, the middle fraction being collected over molecular sieve (Type 4A) and stored under dry nitrogen. Monoglyme was purified by distillation and stored over sodium wire.

Other reagents and solvents were supplied by British Drug House Co. Ltd. and Koch-Light Laboratories Inc. and used without further purification.

CHAPTER NINE

EXPERIMENTAL FOR CHAPTER FOUR - SYNTHESES OF CHLORO- AND FLUORO-1,2,3-TRIAZINES

9.1 Trichloro-1,2,3-Triazine

(A) Preparation of Starting Materials

(i) Pentachlorocyclopropane

Sodium trichloroacetate (108g, 0.58 mole) in 500 ml. of trichloroethylene was mechanically stirred and heated to a gentle reflux for 2 hrs. During this time approximately 1 ml. of water was collected in a Dean Stark trap. After the trap was removed, 75 ml. of monoglyme was added. The mixture was heated at 90-95°C for three days. The pot mixture gradually darkened and became uniform during this period. The reaction mixture was washed twice with water, diluted HCl, and finally water, and then dried over $CaCl_2$. Trichloroethylene was removed using a rotary evaporator and the residue gave colourless liquid (46g, 0.21 mole, yield 36.2% based on CCl_3Co_2Na) after distillation, bp. 80-85°C (30mm Hg), 174-175°C (760mm Hg); lit.[103] 80-85°C (31mm Hg). Identification was by molecular weight (212, (Cl=35) with five chlorine items).

(ii) Tetrachlorocyclopropene

Pentachlorocyclopropane (120g, 0.56 mole) was added to a solution of KOH (90g, 1.58 mole) in 110 ml. of water. The two phase mixture was slowly stireed magnetically and heated to 83°C where a spontaneous reaction occurred. The temperature was kept between 85°C and 95°C by occasional cooling with air or water and stirring was stopped above 90°C. After 1 hr. the mixture was cooled to 50°C and 100 ml. of cold water

followed by cold HCl (25 ml.), was added. The organic layer was taken up in CH_2Cl_2, washed with water, and dried over $CaCl_2$. Fractionation of the extracts gave 70.6g of tetrachlorocyclopropene[155] (yield 71%) as a colourless liquid. bp. 78°C (15mm Hg), 130-133°C (760mm Hg); lit.[103] 71-72 (98mm Hg). Identification was by the i.r. spectrum (1805 cm^{-1}, 1765 cm^{-1} and 750 cm^{-1}) and molecular weight (176, (Cl=35) with four chlorine atoms).

B. Trichloro-1,2,3-Triazine

Tetrachlorocyclopropene (62.3g, 0.35 mole) and trimethylsilylazide (44.4g, 0.385 mole) were magnetically stirred for 13 hrs. at 90°C under nitrogen. The residue, obtained by evaporation of liquids from the reaction mixture under vacuum, was extracted with dry diethylether in a Soxhlet apparatus to separate blown powdery by-product. The evaporation of diethyl ether from the extracts gave crude trichloro-1,2,3-triazine[157], as brown crystals, which became colourless after sublimation. 21.9g yield 33.9%. mp.109-111°C; lit.[94] 110-112°C. [Found: C, 19.7; Cl, 57.9; N, 22.4%: Calculated for $C_3Cl_3N_3$; C, 19.5; Cl, 57.7; N, 22.8%]. Ultraviolet spectrum; λ_{max}, 238nm (ε=5450), 265 and 316nm (sh). I.r. spectrum No.1 mass spectrum No.1.

9.2 Trifluoro-1,2,3-Triazine

A. Vapour Phase Fluorination

(i) Single Step Reaction

Potassium fluoride, dried at 200°C, was placed in a pyrolysis tube (18mm i.d. x 300mm) which had a glass rod (4mm d.) in the centre. The tube was heated in a furnace at 250°C for 2 hrs. and, after the rod was removed carefully to make a small space along the axis, dried at 600°C for 3 hrs. under vacuum. Trichloro-1,2,3-triazine (5g, 27m mole) sublimed at 60-80°C into the tube under *ca.* 0.1mm Hg and the product was collected in a cold trap attached to the other end of the tube. The temperature of the furnace was maintained at 500°C during this operation (*ca.* 2 hrs.). The product was shown by g.l.c. (Column A) to consist of three components identified as 4,5-dichloro-6-fluoro-1,2,3-triazine (161)(2.1g; 47%) n.m.r. spectrum (^{19}F). Mass spectrum No.2, 5-chloro-4,6-difluoro-1,2,3-triazine (162) (1.6g; 40%) n.m.r. spectrum (^{19}F) No.2 i.r. spectrum No.2. Mass spectrum No.3, and 4,5,6-trifluoro-1,2,3-triazine (163) (0.1g, 3%) ultraviolet spectrum: λ_{max} 231nm (ε=2100), 275nm (ε=788). N.m.r. spectrum (^{19}F) No.3. I.r. spectrum No.3. Mass spectrum No.4.

Temperature dependence of the composition of the components in product is visualized in Figure 9.1.

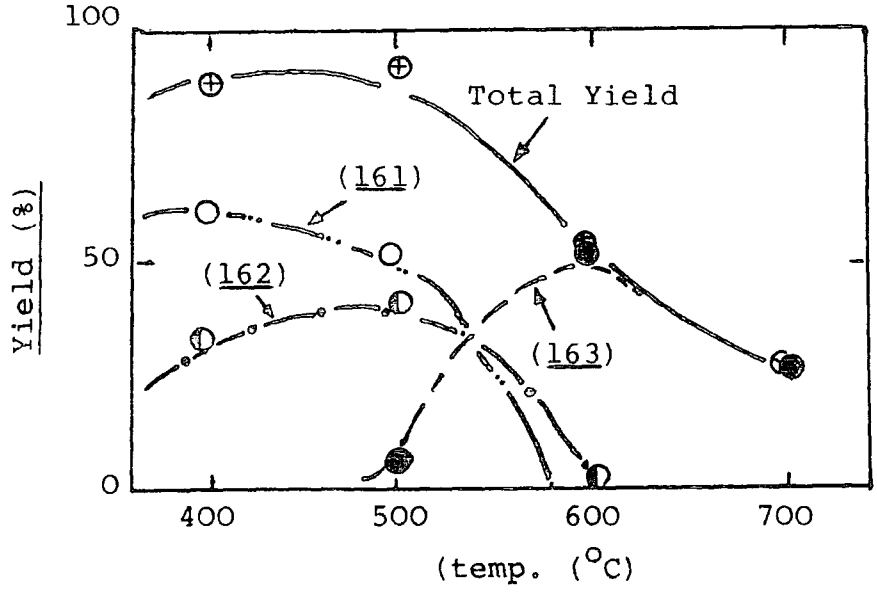


Figure 9.1 Relationship between the composition of the components in product and temperature of the furnace.

(ii) Stepwise Procedure

The product obtained at 500°C, described in (i), was introduced in the tube at 600°C for a period up to 1 hr. The final product contained 4-chloro-5,6-difluoro-1,2,3-triazine (162)(0.63g, 15.3%) and trifluoro-1,2,3-triazine(163) (2.52g, 68.9%). The results of stepwise fluorination at different temperatures are summarized in Table 9.1.

TABLE 9.1 The results of stepwise fluorination (vapour phase)

Temp. (°C)		Yield (%)		
Step One	Two	(163)	(162)	Other Unknown
450	700	54.8	3.6	5
450	600	65.2	17.6	2
500	500 x 3 times	18.3	65.3	0
500	600	69.3	15.5	2

(B) Attempted Solid Phase Fluorination

Trichloro-1,2,3-triazine (157) (1.5g, 8.1 mmole) and dried KF (3.3g, 57 mmole) were poured into a Carius tube (30 ml. volume). The tube was sealed under vacuum (0.01mm Hg) and heated at 180°C for 18 hrs. The product was shown by g.l.c. (Column A) to contain 4,5-dichloro-6-fluoro-1,2,3-triazine (161) (0.11g, 8.5%) and 5-chloro-4,6-difluoro-1,2,3-triazine (162) (0.72g, 58.2%), together with a small amount of trichloroacrylonitrile (34). (Identification: See 11.1(A)). The results of the attempts, using the same procedure, are summarized in Table 9.2.

TABLE 9.2 The results of solid phase fluorination (in Carius tubes)

Temp. (°C)	Product (yield %)		
	(161)	(162)	(34)
150	48.6	11.2	1
180	8.5	58.2	1.3
200	0	37	0.7
270	(greasy product M=421)		

C. Attempted Liquid Phase Fluorination

Trichloro-1,2,3-triazine (157) (0.55g, 3 mmole) and KF (1.67g, 29 mmole) were placed in 10 ml. r.b. flask and sulpholane (3.5 ml.) was introduced under dry N_2 stream. The flask was heated at 80°C for 20 hrs. No volatile product was recovered from the solution. The same procedure was adopted with dodecyltrimethylammonium bromide (surfactant) 0.16g. The volatile product, obtained after vacuum transfer, was shown by g.l.c. (Column A) to contain 4,5-dichloro-6-

fluoro-1,2,3-triazine (161) (0.09g, 17.9%) and 5-chloro-4,6-difluoro-1,2,3-triazine (162) (0.07g, 15.4%). The effects of varying conditions are shown in Table 9.3.

TABLE 9.3 The results of liquid phase fluorination

(157)/ KF (g)	/sulpholane/surfactant (ml)	(g)	Condition	Product (yield %) (161)	(162)
0.55 / 1.67	/ 3.5 /	0.16	80°Cx20hrs.	17.9	15.4
2.00 / 4.5	/ 14.0 /	0.65	20 x 20	0	0
0.55 / 1.67	/ 4.0 /	0.16	130 x 16	4.5	14.3
1.10 / 3.40	/ 8.0 /	0.30	130 x 16	3.5	5.0

9.3 Polyfluoroalkyl-1,2,3-Triazines

(A) Standard Procedure

The experiments described here are attempts at polyfluoroalkylation of trihalogeno-1,2,3-triazines. The experimental procedure, developed by previous workers in these laboratories, was employed.

The required quantities of dry alkali metal fluoride, dry aprotic solvent and trihalogeno-1,2,3-triazine were rapidly introduced into a baked r.b. flask, fitted with a gas-tap and variable volume reservoir, against a flow of dry nitrogen. The apparatus was evacuated and then filled with the requisite amount of gaseous perfluoropropene to equilibriate it to atmospheric pressure. The mixture was vigorously stirred and on completion of reaction, *i.e.* collapse of the hexafluoropropene reservoir, the product was vacuum transferred at temperatures up to 150°C, into a trap cooled by liquid air.

(B) Polyfluoroalkylation of Trichloro-1,2,3-Triazine

The reactions carried out are summarized in Table 9.4 and a typical experiment is described below.

Trichloro-1,2,3-triazine (0.55g, 3 mmole), dry caesium fluoride (2.7g, 17.8 mmole), tetraglyme 10 ml. and hexafluoropropene (3.0g, 20 mmole), were stirred at room temperature for 5 days by which time the reservoir had collapsed. A volatile product (2.8g), isolated by vacuum transfer and separated as a lower layer from tetraglyme, was shown by g.l.c. (Column K) to contain three components besides hexafluoropropene oligomers. Separation by preparative g.l.c. (Column K, 115°C) gave perfluoro-4,6-bisisopropyl-1,2,3-triazine (164), as colourless crystals, (0.32g, 24.7%), mp. 52.0-53°C, [Found: C, 24.5; F, 65.5; N, 10.0%: Calculated for $C_9F_{15}N_3$; C, 24.8; F, 65.5 N, 9.7%] ultraviolet spectrum: λ_{max} 206nm (ε=1700), 246nm (ε=1520 (292nm (420). N.m.r. spectrum (^{19}F) No.4. i.r. spectrum No.4. Mass spectrum No.5, perfluorotrisisopropyl-1,2,3-triazine (165), a yellow liquid, (0.33g, 19.2%), bp. 163-165°C [Found: C, 24.7; F, 67.9; N, 7.5%: Calculated for $C_{12}F_{21}N_3$; C, 24.6; F, 68.2; N, 7.2%]. Ultraviolet spectrum: λ_{max} 231nm (ε=2300), 300 and 346nm (sh). N.m.r. spectra (^{19}F and ^{13}C) No.5. I.r. spectrum No.5. Mass spectrum No.6, and perfluoro-2,4,6-triisopropyl-5-isopropylidene-1,2,3-triazacyclohexa-3,6-diene (166) a yellow liquid (0.1g, 4.5%), bp. 195-197°C [Found: C,24.6; F, 7).1; N, 5.3%: Calculated for $C_{15}F_{27}N_3$; C, 24.5; F, 69.8; N, 5.7%]. Ultraviolet spectrum: λ_{max} 288nm (ε=7300). N.m.r. spectra (^{19}F, ^{13}C and ^{15}N) No.6. I.r. spectra No.6. Mass spectrum No.7.

TABLE 9.4 Polyfluoroalkylation of trichloro-1,2,3-triazine (167)

(157)* (g)	Metal Fluoride (g)	Solvent	Conditions	Product (Yield)		
				(164)	(165)	(166)
0.55	CsF(2.7)	Tetraglyme	25°Cx5 days	24.7	19.2	4.5
0.55	CsF(2.7)	Tetraglyme	25°Cx2 days +60°Cx1 day	0.3	0.4	43.9
1.10	CsF(5.5)	Tetraglyme	25°Cx7 days	20.3	12.7	6.5
0.55	KF(1.2)	Tetraglyme	25°Cx7 days	28.2	11.1	2.0
0.55	KF(1.2)	Sulpholane	25°Cx7 days	23.0	8.3	4.2

*The ratio (157)/Hexafluoropropene/Solvent was 1/5.5/18.0 (by weight) in all cases.

Oligomers of hexafluoropropene were identified as dimers and trimers from the molecular weight (300 and 450 respectively).

(C) Polyfluoroalkylation of Trifluoro-1,2,3-Triazine

The same procedure was adopted as in the case of trichloro-1,2,3-triazine except that trifluoro-1,2,3-triazine was introduced in the vessel through vacuum line after addition of a metal fluoride and a solvent. Reactions carried out are summarized in Table 9.5 and a typical experiment is described below. Dry caesium fluoride (0.2g, 0.13 mmole) and sulpholane (1.0 ml.) were placed in a prebaked r.b. flask, into which trifluoro-1,2,3-triazine (0.5g, 3.7 mmoles) was introduced under vacuum. The solution was vigorously stirred at 20°C for 3 days, after a variable volume reservoir had been attached to

TABLE 9.5 Polyfluoroalkylation of trifluoro-1,2,3-triazine (161)

Solvent	Conditions	Product (yield %)		
		(164)	(165)	(166)
Sulpholane	13°C x 3 days	23.5	2.7	7.1
	20°C x 3 days	16.2	4.5	7.8
	40°C x 2 days	5.8	0.8	25.3
	60°C x 2 days	0.3	0.9	26.8
Tetraglyme	30°C x 3 days	4.6	6.7	8.7
Acetonitrile	20°C x 3 days	12.3	3.5	6.5

The ratio (161)/CsF/Hexafluoropropene/Solvent was 1/0.1/5/2 (by weight) in all cases.

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the vessel, by which time hexafluoropropene (2.3g, 15.3 mmole) was consumed. The product was vacuum transferred and shown by g.l.c. (Column K) to consist of three components besides hexafluoropropene oligomers. The components were identified as perfluoro-4,6-bisisopropyl-1,2,3-triazine (164) (0.26g, 16.2%), perfluorotrisisopropyl-1,2,3-triazine (165) (0.1g, 4.5%) and perfluoro-2,4,6-trisisopropyl-5-isopropylidene-1,2,3-triazahexa-3,6-diene (166) (0.21g, 7.8%). (Identification: see Section 9.3(A)).

CHAPTER TEN

EXPERIMENTAL FOR CHAPTER FIVE - AN UNUSUAL POLYFLUOROALKYLATION PRODUCT

10.1 Reactions of an unusual product

(A) Cycloaddition reactions

(i) Diazomethane

Perfluoro-2,4,6-trisisopropyl-5-isopropylidene-1,2,3-triazacyclohexa-3,5-diene (166) (0.5g, 0.68 mmoles) and diazomethane ether solution (5 ml., *ca.* 2.4 mmoles) were placed in a r.b. flask at room temperature and then set aside for three days. The product was shown by g.l.c. (Column K) to be mainly one component and recrystallization from Et_2O provided 4,4-bistrifluoromethyl-6,8,10-trisheptafluoroisopropyl-1,2,7,8,9-pentaazaspiro[4,5]deca-2,6,9-triene (167) yellow crystals (0.45g, 85%), mp. 62-63°C. [Found: C, 24.6; H, 0.0; F, 65.7; N, 8.9%: Calculated for $C_{16}H_2F_{27}N_5$; C, 24.7; H, 0.26; F, 66.0; N, 9.0%]. Ultraviolet spectrum: λ_{max}, 242nm (ε=13200). N.m.r. spectra (^{19}F, ^{13}C and ^{1}H) No.7. I.r. spectrum No.7. Mass spectrum No.8.

(ii) Attempted reactions

(a) Phenylazide

Perfluoro-2,4,6-trisisopropyl-5-isopropylidene-1,2,3-triazacyclohexa-3,6-diene(166) (0.31g, 0.4 mmoles), phenylazide (0.5g, 4.2 mmole) and diethylether (5.0 ml.) were stirred in a r.b. flask at room temperature for 5 days under nitrogen. The mixture was analyzed by quantitative g.l.c. (Column K),

mass spectroscopy, and ^{19}F n.m.r. spectroscopy, showing that the starting material (166) remained unchanged.

(b) Dimethylacetylenedicarboxylate

Perfluoro-2,4,6-trisisopropyl-5-isopropylidene-1,2,3-triazacyclohexa-3,5-diene(166) (0.2g, 0.27 mmoles) and dimethyl acetylene-dicarboxylate (0.5g, 3.5 mmoles) were sealed in a Carius tube and heated at 75°C for 5 days. The mixture, analyzed by g.l.c. and ^{19}F n.m.r. spectroscopy, contained unchanged starting material (166).

(c) 2,3-Dimethylbuta-1,3-diene

Perfluoro-2,4,6-trisisopropyl-5-isopropylidene-1,2,3-triazacyclohexa-3,6-diene(166) (0.18g, 0.24 mmoles) and 2,3-dimethylbuta-1,3-diene (1.0g) were sealed in a Carius tube and heated at 75°C for two days. The mixture was shown by g.l.c. and ^{19}F n.m.r. spectroscopy to contain unchaged starting material (166).

(d) Tetramethylethylene

Perfluoro-2,4,6-trisisopropyl-5-isopropylidene-1,2,3-triazacyclohexa-3,5-diene (166) (0.2g, 0.27 mmoles) and tetramethylethylene (1.0g, 11.9 mmole) were sealed in a Carius tube and heated at 75°C for 4 days. The starting material (166) remained unchanged and was detected by g.l.c. and ^{19}F n.m.r.

(B) Reactions with Nucleophiles

(i) Methoxide

Perfluoro-2,4,6-trisisopropyl-5-isopropylidene-1,2,3-triazacyclohexa-3,6-diene (166) (0.51g, 0.7 mmoles) and sodium methoxide/methanol solution (10 ml., 0.7 mmoles as Na) were stirred in a r.b. flask at 40°C for 24 hrs. The product was precipitated from methanol after vacuum transfer and shown by g.l.c. to be one component which was identified as 4,6-bisheptafluoroisopropyl-2,5-bis(2´,-trifluoromethyl-2´-methoxy-3´,3´,3´-trifluoropropyl)-1,2,3-triazacyclohexa-3,6-diene (173) white solid (0.32g, 59%) mp. 35-36°C. [Found: C, 25.9; H, 0.92; F, 63.7; N, 5.76%: Calculated for $C_{17}H_7F_{25}O_2N_3$; C, 26.2; H, 0.9; F, 63.4; N, 5.4%] ultraviolet spectrum: λ_{max}, 243nm (ε=3900), 214 and 265nm (sh). N.m.r. spectra (^{19}F and ^{1}H) No.8. I.r. spectrum No.8. Mass spectrum No.9.

(ii) Triethylamine/H_2O

Perfluoro-2,4,6-trisisopropyl-5-isopropylidene-1,2,3-triazacyclohexa-3,5-diene (0.13g, 0.18 mmoles), triethylamine (0.1g, 1.0 mmoles) and H_2O (5 ml) were mixed in a r.b. flask at room temperature for 30 min., by which time the colour of the starting material became red-brown. The product was extracted by diethylether after addition of dil.HCl, and analyzed by g.l.c. - mass spectroscopy and ^{19}F n.m.r. spectroscopy which showed three components as well as a polymeric tar. A major volatile component was unchanged starting material (166), (*ca.* 0.07g, 55%). It was deduced that one of the other com-

ponents was 2,6-bistrifluoromethyl-1,1,1,6,6,6-hexafluoro-hepta-3,6-dione (172) (5%) from the ^{19}F n.m.r. spectrum (73.8 ppm.(S,12) and 185.0 ppm. (S,2)) and mass spectrum (m/e=389 (parent-fluorine)).

The compound (166) (0.13g, 0.18 mmoles) and triethylamine (0.01g, 0.1 mmoles as an aqueous solution 2 ml) were mixed in an n.m.r. tube at room temperature for 4 hrs. The mixture was analyzed by ^{19}F n.m.r. spectrum and suspected to be perfluoro-2,6-dimethyl-4-isopropylidene-hepta-3,6-dione (171) from the ^{19}F n.m.r. spectrum (62.5 ppm (Sb,6), 75.6 ppm(Sb,6), 77.7 ppm (Sb,6), 179.6 ppm (Sb,2))

(C) Radical Addition Reaction (Acet-aldehyde)

Perfluoro-2,4,6-trisisopropyl-5-isopropylidene-1,2,3-triazacyclohexa-3,6-diene (166) (0.54g, 0.73 mmoles), acetoaldehyde (2.50g, 5.7 mmoles) and 1,1,2-trichloro-1,2,2-trifluoroethane (3.0 g) were sealed in a Carius tube, and then irradiated by γ-ray (^{60}Co) for 3 days at room temperature. The product was shown by g.l.c. (Column K) to contain three components and separation by preparative g.l.c. provided 2,4,6-trisheptafluoroisopropyl-5-{1',1'-bistrifluoromethylacetonyl}-1,2,3-triazacyclohexa-3,6-diene (174) (0.48g, 84%) yellow viscous liquid. [Found: C, 27.2; H, 0.5; F, 65.9; N, 5.4%]. Ultraviolet spectrum: λ_{max}, 21.5nm (ε=4700), 245nm (ε=6400), 268 and 320 nm (sh). N.m.r. spectra (^{19}F and ^{1}H) No.9 I.R. spectrum No.9. Mass spectrum No. 10.

Other unknown components were obtained in 7 and 8% yield.

(D) Attempted hydrolysis by HCl

Perfluoro-2,4,6-trisisopropyl-5-isopropylidene-1,2,3-triazahexa-3,6-diene (166) (0.13g, 0.18 mmoles) and concentrated hydrochloric acid (1.0g) were sealed in a Carius tube and heated at 40°C for 3 days and then 100°C for 2 hrs. The starting material (166) remained unchanged, analyzed by g.l.c. and ^{19}F n.m.r. spectrum.

10.2 Reactions of Perfluorotrisisopropyl-1,2,3-Triazine

(A) Phenyl Metallics

(i) Phenylmagnesiumbromide

Perfluorotrisisopropyl-1,2,3-triazine (165) (0.5g, 0.85 mmoles) and dry diethyl ether (5 ml) were placed in a r.b. flask, which had been purged previously by dry nitrogen. Phenylmagnesiumbromide ether solution (1 ml (0.5M), 0.5 m moles) was introduced into the flask against dry nitrogen stream. The solution was stirred magnetically at room temperature for 24 hrs. After vacuum transfer, the product was shown by g.l.c. to contain unreacted (165) (0.18g), unknown (0.02g) and 2-phenyl-4,6-bis-heptafluoroisopropyl-5-heptafluoroisopropylidene-1,2,3-triazacyclohexa-3,6-diene (169) (0.25g, 71% (Conversion 65%), light brown viscous liquid. [Found: C, 33.5; H, 0.9; F, 59.5; N, 6.2%: Calculated for $C_{18}H_5F_{20}N_3$; C, 33.6; H, 0.8; F, 59.2; N, 6.5%]. Ultraviolet spectrum: λ_{max}, 204 nm (ε=14000), 247nm (ε=5600), 354nm (ε=12300), 498nm (sh). N.m.r. spectra (^{19}F and ^{1}H) No.10. I.r. spectrum No.10. Mass spectrum No.11.

(ii) Phenyl lithium

Perfluorotrisisopropyl-1,2,3-triazine (0.5g, 0.85 mmoles) was placed in a r.b. flask into which phenyl lithium hexane solution (1.0g, (1.9M), 1.9 mmoles) was introduced at -78°C against dry nitrogen stream. On warming up to 0°C, a reaction took place violently and the mixture became dark red. The product, obtained after vacuum transfer, was shown by g.l.c. and ^{19}F n.m.r. spectrum to contain 2-phenyl-4,6-bisheptafluoroisopropylidene-1,2,3-triazacyclohexa-3,6-diene (169) (estimated yield 15%).

(B) Fluoroalkenes

(i) Standard Procedure

The required amount of dry caesium fluoride, tetraglyme, and perfluorotrisisopropyl-1,2,3-triazine (165) were rapidly introduced into a pre-baked r.b. flask, fitted with a gas-tap and variable volume reservoir, against a nitrogen stream. The apparatus was evacuated and filled with the requisite amount of gaseous perfluoroalkene to equilibriate it to atmospheric pressure. The mixture was vigorously stirred at 60°C. Products were transferred under vacuum and analyzed by g.l.c. - mass spectroscopy, and ^{19}F n.m.r. spectroscopy.

(ii) Hexafluoropropene

The standard procedure, described in (i) was adopted. Hexafluoropropene (0.5g, 3.3 mmoles), perfluorotrisisopropyl-1,2,3-triazine (165) (0.3g, 0.51 mmoles), caesium fluoride (0.1g, 0.65 mmoles), and tetraglyme (1.0 ml) were stirred for

8 hrs. The product consisted of unreacted (165) (0.01g) and perfluoro-2,4,6-trisisopropyl-5-isopropylidene-1,2,3-triazacyclohexa-3,6-diene (166) (0.36g, 58%) together with hexafluoropropene oligomers (0.3g).

With oxygen Hexafluoropropene (1.0g, 6.6 mmoles), Oxygen (250ml, 11 mmoles), perfluorotrisisopropyl-1,2,3-triazine (165) (0.2g, 0.34mmoles), caesium fluoride (0.1g, 0.65 mmoles) and tetraglyme (1.0 ml) were stirred for 8 hrs according to the procedure in (i). The product (0.3g) consisted of unreacted (165) (0.045g), perfluoro-2,4,6-trisisopropyl-5-isopropylidene-1,2,3-triazacyclohexa-3,6-diene (166) (0.085g, 34%) and hexafluoropropene oligomers (0.13g) together with multi minor components. (Yields are calculated by the g.l.c. spectrum).

(iii) Perfluorocyclobutene

Perfluorocyclobutene (0.5g, 0.3 mmoles), perfluorotrisisopropyl-1,2,3-triazine (165) (0.5g, 0.85 mmoles), caesium fluoride (0.1g, 0.65 mmoles), and tetraglyme (1.0 ml) were stirred at 60°C for 24 hrs, according to the standard procedure in (i). The product (0.54g) was obtained by vacuum transfer and shown by g.l.c. to contain dimers of perfluorocyclobutene, perfluoro-4,5,6-trisisopropyl-2-(cyclobut-1'-enyl)-1,2,3-triazacyclohexa-3,6-diene (170) (0.46g, 72%), isolated by preparative g.l.c. a colourless solid. mp. 46-47°C. [Found: C,25.1; F, 69.2; N, 5.7%: Calculated for $C_{16}F_{29}N_3$; C, 25.7, F, 68.7; N, 5.6%]. Ultraviolet spectrum: λ_{max}, 262nm (ε=3500), 282nm (sh), N.m.r. spectra (^{19}F and ^{13}C) No.11. I.r. spectrum No.11. Mass spectrum No.12. The products also contained other three unknown components (7, 7 and 9%) whose retention time on g.l.c. (Column K) were longer than (170).

(iv) Dimers of perfluorocyclobutene

The standard procedure in (i) was adopted. A mixture of perfluorocyclobutene and dimers of perfluorocyclobutene (2 and 98% respectively) (0.48g, 1.5 mmoles), perfluorotrisisopropyl-1,2,3-triazine (0.29g, 0.5 mmoles), caesium fluoride (0.23g, 1.5 mmoles) and tetraglyme (1.0 ml) were stirred at room temperature for 3 days. The product (0.67g) was isolated by vacuum transfer and shown by g.l.c. to contain unreacted perfluorotrisisopropyl-1,2,3-triazine (165) (11.7%), perfluoro-4,5,6-trisisopropyl-2-(cyclobut-1'-enyl)-1,2,3-triazacyclohexa-3,6-diene (170) (13.0%), perfluoro-2,4,6-trisisopropyl-5-isopropylidene-1,2,3-triazacyclohexa-3,6-diene (166) (3.1%), dimers and trimers of perfluorocyclobutene (28.7 and 36.5% respectively) and other minor components. Calculated yields were 56.3% (0.16g) for (170) and 13.4% (0.04g) for (166) by taking into account the conversion of (165). Dimers and trimers of perfluorocyclobutene were identified by their mass spectra which showed parent peaks at 324 and 486 respectively. Identification of other components were also by mass spectra.

(v) Hexafluorobut-2-yne

According to the standard procedure in (i), hexafluorobut-2-yne (2.5g, 15.4 mmoles), perfluorotrisisopropyl-1,2,3-triazine (0.4g, 0.68 mmoles), caesium fluoride (0.2g, 0.13 mmoles) and tetraglyme (1.0 ml) were stirred at r.t. for 1 hr, giving highly viscous solution from which a white polymer was isolated by washing with dry ether and shown to be polyhexafluorobut-2-yne by the comparison of its i.r. spectrum

with an authentic sample. No volatile product was recovered from the ether extracts, analyzed by ^{19}F n.m.r. spectrum.

(vi) Hexafluoroacetone

Hexafluoroacetone (2g, 12 mmoles), perfluorotris-isopropyl-1,2,3-triazine (0.24g, 0.41 mmoles), caesium fluoride (0.1g, 0.65 mmoles), and tetraglyme (1.0 ml) were stirred, according to the procedure in (i), at 30°C for 16 hrs. ^{19}F n.m.r. spectrum of the reaction mixture showed those of unreacted starting materials. Then the mixture was stirred at 60°C for 24 hrs. The recovered product (0.1g) was shown to contain perfluoro-2,4,6-trisisopropyl-5-isopropylidene-1,2,3-triazacyclohexa-3,6-diene (166) (94%). The yield was 31%. Identification was by mass spectrum (m/e = 735) and the ^{19}F n.m.r. spectrum.

(vii) Fluoride ion

Perfluorotrisisopropyl-1,2,3-triazine (0.25g, 0.43 mmoles), caesium fluoride (0.1g, 0.65 mmoles) and tetraglyme (1.0 ml) were stirred in a r.b. flask under an atmosphere of nitrogen at 60°C for 12 hrs. The product (0.15g) was isolated by vacuum transfer and shown by g.l.c. to consist of perfluoro-2,4,6-trisisopropyl-5-isopropylidene-1,2,3-triazacyclohexa-3,6-diene (166) 74% and perfluoro-4,6-bisisopropyl-1,2,3-triazine (164) 1.0% (detected by mass spectra). Also contained were unknown two components (m/e = 685 and 512, 15.0% and 12.4% respectively).

CHAPTER ELEVEN

EXPERIMENTAL FOR CHAPTER SIX - PRYOLYSIS

11.1 Trichloro-1,2,3-Triazine

(A) At 180°C

Trichloro-1,2,3-triazine (1.5g) was sealed in a Carius tube under high vacuum (10^{-2}mm Hg) and heated at 180°C for 16 hrs. The product was recovered from the tube by vacuum transfer and was shown by g.l.c. (Column K) to be a single component *i.e.*, trichloroacrylonitrile (34) (0.76g, 60%), A colourless volatile liquid. Identification was by the comparison of the i.r. spectrum with that of an authentic sample.[11] I.r. spectrum No.12.

(B) At 150°C

The same procedure, described in (A), was adopted except that the temperature was 150°C. The products were trichloroacrylonitrile (0.13g, 10.2%) and unchanged trichloro-1,2,3-triazine (1.26g, 84%).

(C) With Hexafluorobut-2-yne

(i) At 200°C

Trichloro-1,2,3-triazine (1.5g, 8.1 mmoles) and hexafluorobut-2-yne (3.0g, 18.5 mmoles) were sealed in a Carius tube under high vacuum and heated at 200°C for 15 hrs. The product was trichloroacrylonitrile (1.0g, 57%), together with unreacted hexafluorobut-2-yne. Identification was by mass spectra (m/e=155 and 162 respectively).

(ii) At 280°C

Trichloro-1,2,3-triazine (0.46g, 25 mmoles) and hexafluorobut-2-yne (2.4g, 14.8 mmoles) were sealed in a Carius tube under high vacuum and then heated at 280°C for 15 hrs. The volatile product (0.8g) was recovered by vacuum transfer and evaporation of volatiles at r.t. and shown to be a multi components mixture, one of which was identified as an adduct by mass spectrum (m/e = 317). A yellow solid product (0.2g), separated from black polymeric product by sublimation, was hexakistrifluoromethylbenzene. (Identification was by the ^{19}F n.m.r. spectrum by the comparison with an authentic sample[149]).

11.2 Trifluoro-1,2,3-Triazine

(A) Static pyrolysis

(i) With Naphthalene

Trifluoro-1,2,3-triazine (0.4g, 3 mmoles) and naphthalene (5.0g) were sealed in a Carius tube under high vacuum and then heated at 330°C for 2 hrs. The volatile product (0.2g) was recovered by vacuum transfer and contained trifluoroacrylonitrile (175) (0.03g, 8%). Identification was by the mass spectrum (No.13) and the ^{19}F n.m.r.[150] and i.r. spectra of the mixture (CN absorption 2250 cm^{-1}),[152] unreacted trifluoro-1,2,3-triazine (163) (0.09g, 23%) and other minor components.

(ii) Without Naphthalene

Trifluoro-1,2,3-triazine (0.37g) were sealed in a Carius tube and heated at 350°C for 4 hrs. The volatile product (0.15g), recovered from the tube covered with a black polymer, contained mainly trifluoro-1,2,3-triazine (163).

(iii) With Hexafluorobut-2-yne

Trifluoro-1,2,3-triazine (0.33g, 2.5 mmoles) and hexafluorobut-2-yne (3.1g, 19 mmoles) were sealed in a Carius tube and heated at 350°C for 15 hrs. The recovered product (0.62g) contained hexafluorobut-2-yne together with multi minor components.

(B) Flash pyrolysis

Trifluoro-1,2,3-triazine was passed through a quartz tube packed with platinum foil at a requisite temperature under 10^{-1} mm Hg and then collected on a cold finger attached to the other end of the tube. The results are listed in Table 11.1.

TABLE 11.1 Flash pyrolysis of trifluoro-1,2,3-triazine

used (g)	Temperature	Product (g)
0.36g	800°C	yellow coloured product, solidified during warming up to r.t., contained the nitrile group (2230 cm^{-1} in the i.r. spectrum).
0.3g	700°C	*c.a.* 0.15g - the same result as above.
0.3g	600°C	trifluoro-1,2,3-triazine was recovered unchanged

11.3 Perfluoro-4,6-Bisisopropyl-1,2,3-triazine

(A) Static Pyrolysis

Perfluoro-4,6-bisisopropyl-1,2,3-triazine (164) (1.5g, 3.4 mmoles) was sealed in a Carius tube under high vacuum ($10.^{-2}$ mm Hg) and heated at 330°C for 2 hrs. The recovered product (1.35g) contained Perfluoro-2,4,5-trisisopropyl-pyrimidine (171) (0.42g, 29.8%), a colourless liquid. [Found: C, 25.8; F, 69.0; N, 5.2%: Calculated for $C_{13}F_{22}N_2$; C, 25.9; F, 69.4; N, 4.7%]. U.v. spectrum, λ_{max} (ε), 256nm (7100), 222nm (4400). N.m.r. spectrum (^{19}F), No.12 I.r. spectrum No.13. Mass spectrum No.14, perfluoro-2,3,6-trisisopropyl-pyridine (178) (0.11g, 7.8%) (Identification: See 12.2(D), perfluoroisobutyronitrile (46) (0.17g, 11.8%) and perfluoro-3-methylbut-1-yne (179) (0.03g, 2.3%) (Identification: See 11.3(B)), perfluoro-2,4,6 ,8-tetrakisisopropyl-1,5-diaza-tricyclo[4,2,0,$O^{2,5}$]octa-2,6-diene (180) (0.07g, 5.2%), (Identification: See 12.2(A)), a dimer of perfluoro-3-methylbut-1-yne (0.02g, 1.2%) (Identification was by mass spectrum 405 (M^+-F) and other unidentified minor components.

(B) Flash Pyrolysis

A certain amount of perfluoro-4,6-bisisopropyl-1,2,3-triazine (164) was sublimed at 40-60°C into a quartz tube (300mm) which had been kept at a required temperature under 10^{-2} mm Hg, and the pyrolysate was collected in a U-shaped trap which was attached to the other end of the tube cooled by liquid air. The results are shown in Table 11.2. Perfluoroisobutyronitrile (46) was identified by the comparison of its spectra with an authentic sample.[10] N.m.r. spectrum

TABLE 11.2 Flash Pyrolysis of (164)

used (mg)	Temperature of the furnace (°C)	Product
500	630	Perfluoroisobutyronitrile (46) quant. Perfluoro-3-methylbut-1-yne (179) quant. (total 460 mg).
50	500	The same products as above (total 4-50 mg).
60	400	Unchanged (164) (83%). (*c.a.* 50 mg.)

(^{19}F) No.13 I.r. spectrum No.14. Mass spectrum (m/e=176, M^+-19(F)). Perfluoro-3-methylbut-1-yne (179) a colourless gas, n.m.r. spectrum (^{19}F) No.14, I.r. spectrum as a mixture with (46) No.15. Mass spectrum No.16.

(C) Reaction of Perfluoro-3-methylbut-1-yne

(i) 2,3-Dimethylbuta-1,3-diene

Perfluoro-3-methylbut-1-yne (179) was prepared as a mixture with perfluoroisobutyronitrile by flash pyrolysis of perfluoro-4,6-bisisopropyl-1,2,3-triazine (0.6g) at 600°C as described in (B) and collected in a U-shaped tube which had contained 2,3-dimethylbuta-1,3-diene (1.0g) at the temperature of liquid air. The U-tube was set aside until warming up to the room temperature and the evaporation of low b.p. material gave a product (0.41g) which was shown by g.l.c. to contain mainly three components and separated by preparative g.l.c. They are 1-fluoro-2-heptafluoroisopropyl-4-methyl-

4-(2'-methyl-prop-2'-enyl)-cyclobut-1-ene (188) (0.29g, 72.3%) a colourless liquid. [Found: C,45.1; H, 3.10; F, 51.8%: Calculated for $C_{11}H_{10}F_8$; C, 44.9; H, 3.4; F, 51.7%]. N.m.r. spectra (^{19}F and ^{1}H) No.15. I.r. spectrum No.16. Mass spectrum No.16, and 1-fluoro-2-heptafluoroisopropylcyclohexa-1,4-diene (189) (0.07g, 18%), a colourless liquid. N.m.r. spectra (^{19}F and ^{1}H) No.16. I.r. spectrum No.17, mass spectrum No.17. The third component (0.04g, 9.8%) was a mixture of four compounds which were identified as $(CF_3)_2CFC{\equiv}CF/CH_2{=}\overset{CH_3}{\overset{|}{C}}{-}\overset{CH_3}{\overset{|}{C}}{=}CH_2{=}^{1}/_{2}$ adducts by molecular weight (m/e=376).

(ii) Attempted Thermal Oligomerization

A mixture of perfluoro-3-methylbut-1-yne (179) and perfluoroisobutyronitrile (46) (total 0.28g molar ratio was 1:1), prepared by flash pyrolysis of perfluoro-4,6-bisisopropyl-1,2,3-triazine (0.3g) at 600°C, was sealed in a Carius tube with carbontetrachloride (1.0g) and heated at 100°C for 24 hrs. The mixture was analyzed by g.l.c. and ^{19}F n.m.r. spectroscopy, showing to contain unchanged starting materials, (46) and (179).

11.4 Perfluoro-Trisisopropyl-1,2,3-Triazine

(A) Static Pyrolysis

Perfluorotrisisopropyl-1,2,3-triazine (0.2g) was sealed in an n.m.r. tube under 10^{-2}mm Hg and heated at 200°C for 1 hr. The product (0.19g) consisted of perfluoroisobutyronitrile (46) and perfluoro-2,5-dimethylhex-3-yne (45). N.m.r. spectrum No.17, I.r. spectrum No.18. Mass spectrum (m/e=343, M^+-19(F)), identified by the comparison with an authentic sample [10].

(B) Flash Pyrolysis

Perfluorotrisisopropyl-1,2,3-triazine (0.2g) was evaporated into a quartz tube heated at 600°C under 10^{-1}mm Hg and collected in a cold trap. The product (0.18g) contained perfluoroisobutyronitrile (46) and perfluoro-2,5-dimethylhex-3-yne)45). (Identification was by ^{19}F n.m.r. spectrum of the mixture).

11.5 Perfluoro-2,4,6-Trisisopropyl-5-Isopropylidene-1,2,3-Triazacyclohexa-3,6-diene

(A) Static Pyrolysis

Perfluoro-2,4,6-trisisopropyl-5-isopropylidene-1,2,3-triazacyclohexa-3,6-diene (166) (3.0g, 4 mmoles) was sealed in a Carius tube under 10^{-2} mm Hg and heated at 350°C for 4 hrs. The product (2.8g) contained five components, one of which (0.33g) was not identified. They are perfluoro-4-isopropyl-2,5-dimethylhexa-2,3-diene (193) (1.23g, 60%), a colourless liquid, b.p. 105-107°C. [Found: F, 73.74%: Calculated for $C_{11}F_{20}$; F, 74.22%]. N.m.r. spectra (^{19}F and ^{13}C) No.18. I.r. spectrum No.19. Mass spectrum No.18, perfluoro-4,5-bisisopropyl-2,8-dimethylocta-2,3,5,6-tetraene (194) and perfluoro-6-isopropyl-2,5,5,8-tetramethylnona-6,7-diene-3-yne (195) (0.70g, 13 and 12% respectively), colourless liquids, N.m.r. spectra (^{19}F). Nos. 19 and 20 respectively. I.r. spectrum as a mixture No.20. Mass spectrum as a mixture No.19, and perfluoroisobutyronitrile (46) (0.54g, 68%) (Identification was by ^{19}F n.m.r. spectrum and mass spectrum (m/e = 176 (M^+-F)).

(B) Isomerization of perfluoro-6-isopropyl-2,5,5,8-tetramethylnona-6,7-diene-3-yne (195) to perfluoro-4,5-diisopropyl-2,8-dimethylocta-2,3,5,6-tetraene (194)

A mixture of (194) and (195) (0.5g, molar ratio was 52:48) was sealed in an n.m.r. tube under 10^{-2} mm Hg and heated at 400°C for 1 hr. The product was perfluoro-4,5-diisopropyl-2,8-dimethylocta-2,3,5,6-tetraene (194) identified by ^{19}F n.m.r. spectrum.

CHAPTER TWELVE

EXPERIMENTAL FOR CHAPTER SEVEN - PHOTOLYSIS

12.1 Trifluoro-1,2,3-Triazine

(A) Vapour phase

Trifluoro-1,2,3-triazine (0.25g) was sealed in a quartz tube (vol.20 ml) under 10^{-2}mm Hg and irradiated at 253.7nm for 7 days. A light brown polymer (*c.a.* 0.15g) was formed on the surface of the tube, which was not soluble in acetone chloroform, methylenedichloride, carbontetrachloride and acetonitrile. Poly(trifluoroazete) (201). [Found: C, 31.1; F, 50.2; N, 16.0%: Calculated for C_3F_3N : C, 33.6; F, 53.3; N, 13.1%]. I.r. spectrum No.21.

(B) Liquid phase

Trifluoro-1,2,3-triazine (1.0g) and 1,1,2-trichloro-1,2,2-trifluoroethane (23ml) were sealed in a quartz tube (vol.50ml) and then irradiated at 253.7nm for 48 hrs. A light brown polymer was formed on the surface. The component in the liquid phase was unchanged trifluoro-1,2,3-triazine (163). (Identification by the ^{19}F n.m.r. spectrum of the solution).

(C) With Hexafluorobut-2-yne

Trifluoro-1,2,3-triazine (0.4g, 2.96 mmoles) and hexafluorobut-2-yne (1.9g, 11.7 mmoles) were sealed in a quartz tube (300ml) and then irradiated at 253.7nm for 63 hrs. A light brown polymer (*c.a.* 0.2g) was formed on the surface of

the tube and identified as poly(trifluoroazete-co-hexafluorobut-2-yne) (202). I.r. spectrum No.22, mass spectrum No.20.

(D) With Hexafluorobut-2-yne in a large vessel

Trifluoro-1,2,3-triazine (1.5g, 11.1 mmoles) and hexafluorobut-2-yne (7g, 43.2 mmoles) were sealed in a quartz vessel (31) and irradiated at 253.7nm for 6 hrs. The liquid product was recovered by vacuum transfer and evaporation of the remaining gaseous components and shown to be a multi components mixture. No absorption was observed above 2000cm^{-1} in its i.r. spectrum. One of the components was obtained in 5% yield (calculated by the g.l.c. spectrum) and had molecular weight 269 (mass spectrum No.21).

12.2 Perfluoro-4,6-Bisisopropyl-1,2,3-Triazine

(A) Liquid Phase

Perfluoro-4,6-bisisopropyl-1,2,3-triazine (1.0g, 2.3 mmoles) and 1,1,2-trichloro-1,2,2-trifluoroethane (15g) were sealed in a quartz tube under high vacuum and irradiated at 253.7nm (low pressure arcs) for 8 hrs. The product (0.93g) was obtained by evaporation of the solvent under reduced pressure (20mm Hg) and contained a single component which was identified as perfluoro-2,4,6-8-tetrakisisopropyl-1,5-diazatricyclo[4,2,0,$O^{2,5}$]octa-3,7-diene (180) (99.3%), a colourless viscous liquid. [Found: C, 26.7; F, 69.8; N, 3.6%: Calculated for $C_{18}F_{30}N_2$: C, 26.5; F, 70.0; N, 3.4%] N.m.r. spectrum (^{19}F) No.21, I.r. spectrum No.23. Mass spectrum No.22.

(B) Vapour Phase

Perfluoro-4,6-bisisopropyl-1,2,3-triazine (0.3g, 0.7 mmoles) was sealed in a quartz tube (300 ml) under 5 x 10^{-2} mm Hg and then irradiated by low pressure arcs (253.7nm) for 95 hrs. The product (0.16g) was recovered by vacuum transfer and contained three components in 3.1%, 4.2% and 90.6%. The main component was perfluoro-2,4,6,8-tetrakisisopropyl-1,5-diazatricyclo[4,2,0,$0^{2,5}$]octa-3,7-diene (180) (yield 57%), and one of the minor components (3.1%) was perfluoroisobutyronitrile (46) (yield 3.7%). (Identification was by n.m.r. spectroscopy).

(C) Cophotolysis

(i) Trifluoro-1,2,3-triazine

Perfluoro-4,6-bisisopropyl-1,2,3-triazine (0.3g, 0.69 mmoles), trifluoro-1,2,3-triazine (0.4g, 3.0 mmoles) and 1,1,2-trichloro-1,2,2-trifluoroethane (5.0g) was sealed in a quartz tube (20 ml) under 10^{-2}mm Hg and irradiated at 253.7nm for 24 hrs. The product (0.24g) was obtained by evaporation of the solvent under reduced pressure and shown by g.l.c. to contain three components A, B and C in 6, 80 and 14% respectively which were identified as trifluoro-1,3,5-triazine (210)[206]. ^{19}F n.m.r. spectrum (30-34 p.p.m. multiplet). Mass spectrum, m/e=135 (without loss of N_2), perfluoro-2,4-bisisopropylpyridine (209)[205] (0.17g, 53%) a colourless liquid. ^{19}F n.m.r. spectrum No.22. I.r. spectrum No.24. Mass spectrum (m/e=469) and perfluoro-2,4,6,8-tetrakisisopropyl-1,5-diazatricyclo[4,2,0,$0^{2,5}$]octa-3,7-diene (180) by the comparison with authentic samples. (Iso-

lation was by preparative g.l.c.).

(ii) Furan

Perfluoro-4,6-bisisopropyl-1,2,3-triazine (0.35g, 0.8 mmoles), furan (2.0g, 29.4 mmoles) and 1,1,2-trichloro-1,2,2-trifluoroethane (5.0g) were sealed in a quartz tube (20 ml) under 10^{-2}mm Hg and irradiated by low-pressure arcs (253.7nm) for 9 hrs. The product (0.34g) was obtained by filtration of a polymeric product and evaporation of the remaining low b.p. materials under reduced pressure and consisted mainly of three components, two of which have the same retention time on Column K (g.l.c.). They were (endo) 2-fluoro-3,4-bisheptafluoroisopropyl-4-aza-9-oxatricyclo[4,2,1,$O^{2,5}$]nona-3,7-diene (212) and (endo) 1-fluoro-7,9-bisheptafluoroisopropyl-8-aza-3-oxatricyclo[5,2,0,$O^{2,6}$]nona-4,8-diene (213) (0.21g, 34% and 21% respectively), a colourless liquid. N.m.r. spectra (^{19}F and ^{1}H) No.23, and No.24. I.r. spectrum as a mixture, No.25. Mass spectrum as a mixture, No.23, and (endo) 9-fluoro-1,8-bisheptafluoroisopropyl-7-aza-3-oxatricyclo[5,2,0,$O^{2,5}$]nona-4,8-diene (214) (0.05g, 13%), a colourless liquid. N.m.r. spectra (^{19}F and ^{1}H) No.25, I.r. spectrum No.25, mass spectrum No.24.

(D) Pyrolysis of Perfluoro-2,4,6,8-tetrakisisopropyl-1,5-diazatricyclo[4,2,0,$O^{2,5}$]octa-3,7-diene (180)

The compound (180) (0.2g) was sealed in a melting point tube and heated at 350°C for 1 hr. The product was examined by ^{19}F n.m.r. spectroscopy (capillary method) and shown by g.l.c. (Column O) to contain two components which were

perfluoro-2,4,6-trisisopropylpyridine (204)[195] (yield 98.6%) a colourless liquid. N.m.r. spectrum (^{19}F) No.26, I.r. spectrum No.27, mass spectrum (m/e=619) and perfluoroisobutyronitrile (46) (*c.a.* 100%). (Identification was by the comparison with authentic samples).

(E) Other Attempts

(i) Trapping of Perfluoro-2,4-bisisopropylazete (181)

Perfluoro-4,6-bisisopropyl-1,2,3-triazine (164), a trapping reagent, and 1,1,2-trichloro-1,2,2-trifluoroethane were sealed in a quartz tube and irradiated at 253.7nm for 6-8 hrs. The products were examined by ^{19}F n.m.r. and g.l.c.-mass spectrometry. The results are shown in Table 12.1.

TABLE 12.1 Attempted Trapping of the Azete (181)

(164) g (mmoles)	Trapping reagent g (m moles)	Product (yield %)
0.12, (0.28)	Hexafluorobut-2-yne 1.6 (10)	The dimer (180) (quant.)
0.36 (0.83)	Perfluoro-3-methylbut-1-yne 0.22 (1.0) and Perfluoroisobutyronitrile 0.20 (1.0)	The dimer (180) (quant.)
0.35 (0.80)	2,3-dimethylbut-2-ene 1.0 (11.9)	The dimer (180) (48%) a 1:1 adduct of (181) with the dimethylbutene was detected (m/e=491) (3%)

(ii) Photolysis of Perfluoro-2,4,6,8-Tetrakisisopropyl-1,5-diazatricyclo[4,2,0,$O^{2,5}$]octa-3,7-diene (180)

The compound (180) 0.1g and 1,1,2-trichloro-1,2,2-trifluoroethane (1.0g) were sealed in a quartz n.m.r. tube

and irradiated at 253.7nm for 2 days. The ^{19}F n.m.r. spectrum of the solution showed that the starting material remained unchanged.

12.3 Perfluorotrisisopropyl-1,2,3-triazine

(A) Vapour Phase

Perfluorotrisisopropyl-1,2,3-triazine (0.16g, 0.27 mmoles) was sealed in a quartz tube (25 ml) under high vacuum (10^{-2}mm Hg) and irradiated at 253.7nm for 72 hrs. The product (0.14g) was shown to contain perfluoroisobutyronitrile (46) (5.2%), perfluoro-2,5-dimethylhex-3-yne (45) (28.5%) and unchanged perfluorotrisisopropyl-1,2,3-triazine (164) (64%).

(B) Liquid Phase

Perfluorotrisisopropyl-1,2,3-triazine (0.2g, 0.34 m moles) and 1,1,2-trichloro-1,2,2-trifluoroethane (2 ml) were sealed in a quartz n.m.r. tube under high vacuum and irradiated at 253.7nm for 4 hrs. The product consisted of perfluoro-2,5-dimethylhex-3-yne (45) and perfluoroisobutyronitrile (46). (Identification was by the ^{19}F n.m.r. spectrum of the solution).

12.4 Low Temperature Photolysis

(A) Direct Observation of Intermediates

(i) Apparatus and Procedure

An infrared cell for low temperature study was equipped with a quartz window for irradiation (Fig. 12.1).

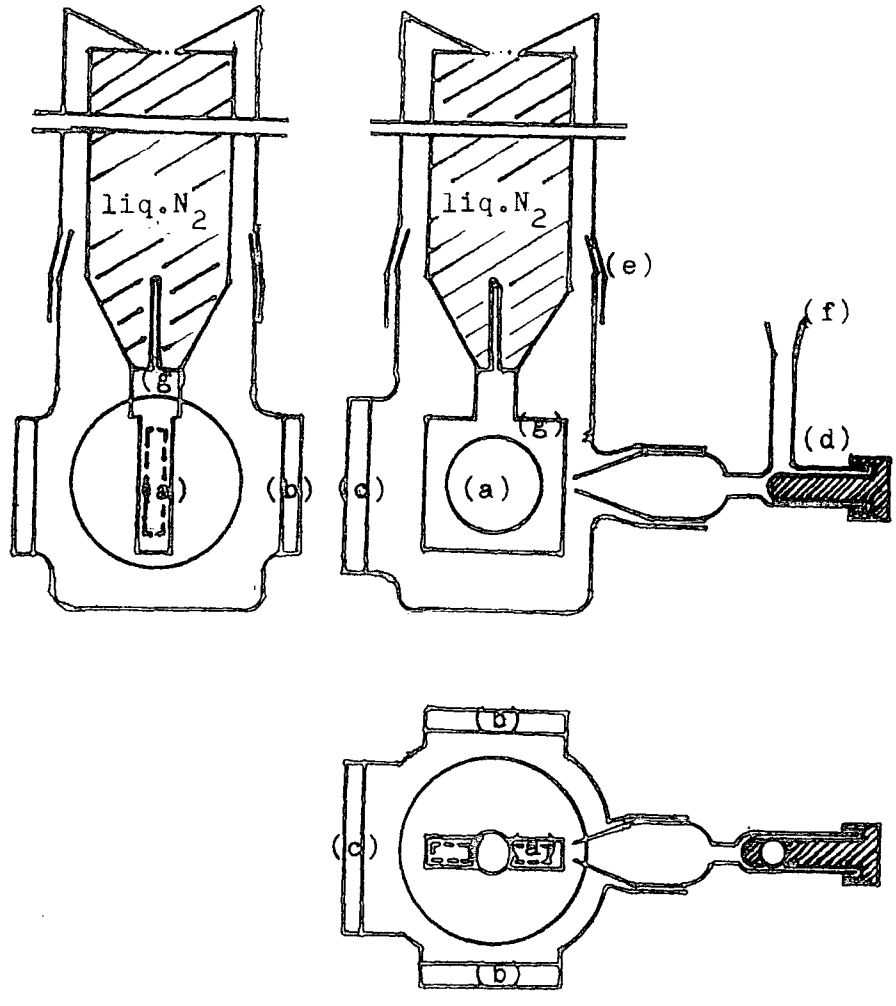
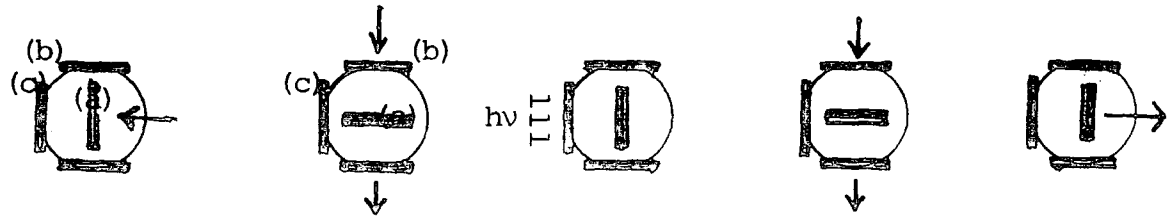


Figure 12.1 Apparatus for Low temperature photolysis

(a) KBr plate on which samples are deposited at 77K, (b) KBr window for measurement of i.r. spectra, (c) quartz window for photolysis, (d) tap for evacuation of cell and introduction of samples on the KBr plate, (e) joint for rotation of the KBr plate, (f) connection to mass spectrometer, (g) KBr plate holder (Copper).



(1) Introduction of a sample

(2) Observation of i.r. spectrum

(3) Photolysis

(4) Observation of i.r. spectrum of the photolysate

(5) Recording of mass spectrum of the photolysate

Figure 12.2 Procedure (position of KBr plate).

The standard procedure is the above Figure 12.2.

After evacuation of the cell was carried out under high vacuum ($< 10^{-2}$mm Hg), the reservoir was filled with liquid nitrogen (afterwards every 20 min.). The cell was kept under high vacuum for 1.5 hrs and then a sample was introduced through vacuum line. The amount of the sample deposited on the KBr plate at 77K was adjusted by trial and error so as to obtain the i.r. spectrum with proper intensity of absorptions. The cell was evacuated again to high vacuum ($< 10^{-2}$mm Hg) and the deposited sample was irradiated using low pressure arcs (253.7nm). After photolysis was completed (monitored by i.r. spectroscopy), the cell was connected to a mass spectrometer and allowed to warm up to room temperature gradually, replacing the liquid nitrogen in the reservoir by ethanol (cooled by dry ice). When the temperature of the reservoir was -40°C, the first mass spectrum was recorded and then other spectra were observed at higher temperatures.

(ii) Trifluoro-1,2,3-Triazine

Trifluoro-1,2,3-triazine was irradiated for 2-4 hrs. according to the procedure described in (i). The product was identified as a mixture of trifluoroazete (175), perfluoro-2-azabicyclo[2,2,0]hexa-2,5-diene (215), and unchanged trifluoro-1,2,3-triazine (163), I.r. spectrum as a mixture No.28,and No.29 for trifluoro-1,2,3-triazine at 77K. Mass spectrum No.25 for (175). (215): m/e = 169.

(iii) Perfluoro-4,6-Bisisopropyl-1,2,3-triazine

Perfluoro-4,6-bisisopropyl-1,2,3-triazine was irradiated for 2 hrs. according to the procedure described in (i). The product was identified as a mixture of monomeric and dimeric species derived from perfluoro-2,4-bisisopropylazete (181). I.r. spectrum (at 77K) No.30 and perfluoro-2,4,6,8-tetrakisisopropyl-1,5-diazatricyclo[4,2,0,$O^{2,5}$]octa-3,7-diene (180) at 77K, No.31. Mass spectra No.26 and No.27 for monomeric and dimeric species respectively.

(iv) Perfluorotrisisopropyl-1,2,3-Triazine

Perfluorotrisisopropyl-1,2,3-triazine was irradiated for 1 hr. according to the standard procedure in (i). The product was identified as a mixture of perfluoroisobutyronitrile (46) and perfluoro-2,5-dimethylhexa-3-yne (45). I.r. spectrum (at 77K) No.33. Mass spectra, m/e=175 (M^+(46)-F) and 343 (M^+(45)-F).

(B) Attempted Isolation of Photolysate

(i) Apparatus

Apparatus for preparative scale low temperature

photolysis are shown in Figures 12.3 and 12.4. Both are designed for external irradiation.

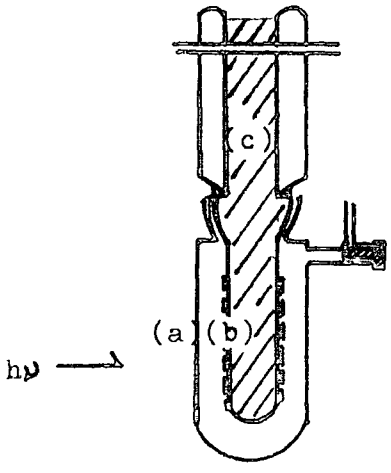


Fig.12.3 Apparatus for solid phase photolysis at 77K.

(a) quartz tube for irradiation.

(b) pyrex tube on which thin film of the sample was formed

(c) liq. N_2 reservoir

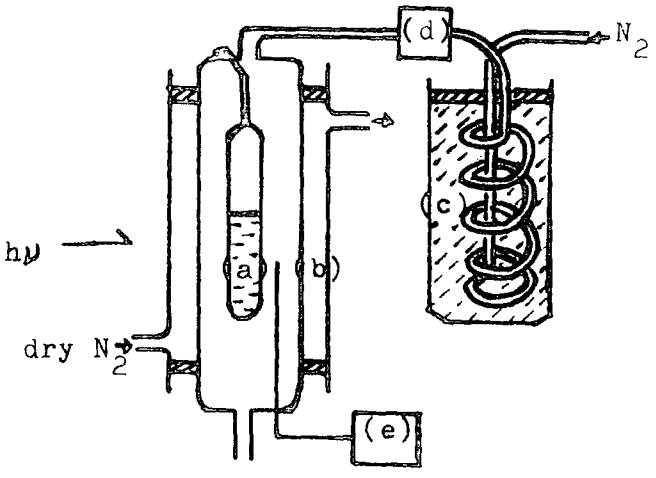


Fig.12.4 Apparatus for photolysis in an organic glass.

(a) sample in solvent

(b) quartz jacket where dry nitrogen passes

(c) liq. N_2 reservoir

(d) temperature controller

(e) thermometer.

(ii) Solid phase photolysis

Perfluoro-4,6-bisisopropyl-1,2,3-triazine (0.3g) was placed in the apparatus (Fig.12.3) whose atmosphere was then replaced by dry nitrogen. The outer tube was cooled in liquid air and evacuation of the system was carried out under high vacuum (10^{-2}mm Hg). The inner tube was cooled by filling the reservoir with liquid nitrogen after the outer tube was warmed up to *c.a.* 40°C. Thin film of the triazine

(164) was formed on the surface of the inner tube. The film was irradiated at 253.7nm for 36 hrs. at 77K. The photolysate (0.26g) was dissolved in 1,1,2-trichloro-1,2,2-trifluoroethane for recovery and consisted of three components which have similar retention time on Column K and identified as perfluoro-2,4,6,8-tetrakisisopropyl-1,5-diazatricyclo-[4,2,0,$O^{2,5}$]octa-3,7-diene (180) (70%) and perfluoro-2,4,6,8-tetrakisisopropyl-3,7-diazabicyclo[4,2,0]octa-2,4,7-triene (206) (23%). N.m.r. spectrum (^{19}F) No.27. I.r. spectrum (as a mixture with (180) and (217)) No.32, and an unknown dimer (217) (4%). (Mass spectra are identical to (180): m/e=745 (M^+-CF_3)).

(iii) Photolysis in an Organic Glass

Perfluoro-4,6-bisisopropyl-1,2,3-triazine (0.1g) and 1,1,2-trichloro-1,2,2-trifluoroethane (2ml) were sealed in a quartz tube (5 ml) under 10^{-2}mm Hg and irradiated at -30°C for 18 hrs. using low pressure arcs (253.7nm) and the apparatus (Fig.12.4). The photolysate contained perfluoro-2,4,6,8-tetrakisisopropyl-1,5-diazatricyclo[4,2,0,$O^{2,5}$]octa-3,7-diene (180) (67%) and perfluoro-2,4,6,8-tetrakisisopropyl-3,7-diazabicyclo[4,2,0]octa-2,4,7-triene (206) (27%) and other unknown minor components.

(iv) I.R. measurement at 77K

Infrared spectra of perfluoro-2,4,6,8-tetrakisisopropyl-1,5-diazatricyclo[4,2,0,$O^{2,5}$]octa-3,7-diene (180) and its mixture with perfluoro-2,4,6,8-tetrakisisopropyl-3,7-diazabicyclo[4,2,0]octa-2,4,7-triene (206) and an unknown

dimer (217) were observed at 77K using the low temperature cell. They were identical to those observed at r.t.

(v) Photolysis of the dimer (180) at 77K

The dimer (180) was irradiated for 4 hrs. according to the procedure described in 12.4(A)(i). The i.r. spectrum remained unchanged.

CHAPTER THIRTEEN

EXPERIMENTAL FOR CHAPTER EIGHT - NUCLEOPHILIC REACTION

13.1 Substituted ethylenes

(A) 2,3-Dimethylbut-2-ene

Perfluorotrisisopropyl-1,2,3-triazine (0.4g, 0.7 mmoles) and 2,3-dimethylbut-2-ene (1.5g, 17.9 mmoles) were sealed in a Carius tube (15 ml) and heated at 70°C. The colour of the mixture turned to green from light yellow after 3 hrs. The tube was kept at 70°C for 4 days. The product (0.41g) contained 2-(1',2'-dimethylprop-1'-enyl)-2-methyl-4,5,6-tris-heptafluoroisopropyl-1,3-diaza-2-azaniacyclohexadienide (220) (89%), a green liquid. [Found: C, 32.7; H, 1.63; F, 59.0; N, 6.54%: Calculated for $C_{18}H_{12}F_{21}N_3$; C, 32.2; H, 1.8; F, 59.6; N, 6.3%]. U.v. spectra: $\lambda_{max}(\varepsilon)$,213 nm (2700), 248nm (5170), 294nm (4090) in acetonitrile; 218nm (3600), 247nm (8200), 292nm (6200) 398nm (30) in cyclohexane,n.m.r. spectra (^{19}F, ^{1}H and ^{13}C) No.28. I.r. spectrum No.34, mass spectrum No.28 and unreacted perfluorotrisisopropyl-1,2,3-triazine (8%), and an unknown component (3%).

(B) 2-Methylbut-2-ene

Perfluorotrisisopropyl-1,2,3-triazine (0.5g, 0.85 m moles) and 2-methylbut-2-ene (2.0g, 28.6 mmoles) were sealed in a Carius tube (15ml) under 10^{-2}mm Hg and heated at 70°C. The colour of the mixture turned to green from light yellow after 3 days. The tube was kept at 70°C for 4 days. The product consisted of mainly three components which were identified as 2-(2'-methylprop-1'-enyl)-2-methyl-4,5,6-trishepta-

fluoroisopropyl-1,3-diaza-2-azaniacyclohexadienide (222) (56%) a deep green liquid, [Found: C, 31.8; H, 1.3; F, 60.2; N, 6.7%: Calculated for $C_{17}H_{10}F_{21}N_3$: C, 31.1; H, 1.5; F, 60.9; N, 6.4%] U.v. spectra: λ_{max} (ε), 248nm (4370), 302nm (6550), 392nm (160) in acetonitrile; 244nm (5960), 298nm (5200, 404nm (300), in cyclohexane. N.m.r. spectra (^{19}F, ^{1}H and ^{13}C) No.30. I.r. spectrum No.36, mass spectrum No.29 and 2-(1'-methylprop-1'-enyl)-1-methyl-4,5,6-trisheptafluoroisopropyl-1,2,3-triazacyclohexa-3,5-diene (223) (33%) a slightly yellow liquid. N.m.r. spectra (^{19}F and ^{1}H) No.32. I.r. spectrum No.38. Mass spectrum No.30 and unreacted perfluorotrisisopropyl-1,2,3-triazine (165) (7 %), together with an unknown component (4%).

(C) 3,3-dimethylpropene

Perfluorotrisisopropyl-1,2,3-triazine (0.18g, 0.3 m moles) and 3,3-dimethylpropene (0.35g, 4.2 mmoles) were sealed in a Carius tube (15 ml) and heated at 70°C for 2 weeks then at 100°C for 2 days. The triazine remained unchanged (detected by ^{19}F n.m.r. spectrum and g.l.c. analysis). Then the mixture was heated at 200°C for 3 hrs. The product was shown to contain perfluoroisobutyronitrile (45) and perfluoro-2,5-dimethylhex -3-yne (46) (by ^{19}F n.m.r. spectroscopy).

(D) Addition Reaction of Bromine

(i) The Adduct (221)

2-(1′,2′-Dimethylprop-1′-enyl)-2-methyl-4,5,6-trisheptafluoroisopropyl-1,3-diaza-2-azaniacyclohexadienide (220) (0.2g, 0.3 mmoles) and carbontetrachloride 2g. were placed in an n.m.r. tube in which bromine (1.0g, 6.2mmoles) was introduced. The solution was heated up to boiling point for *ca.* 5 min.

The residue contained one component identified as 2-(1′,2′-dibromo-1′,2′-dimethylpropyl)-2-methyl-4,5,6-trisheptafluoroisopropyl-1,3-diaza-2-azaniacyclohexadienide (221), a slightly yellow viscous liquid. U.v. spectrum: λ_{max} (ε), 251.2nm (10300), 296.2nm (6730), N.m.r. spectra (^{19}F and ^{1}H) No.29. I.r. spectrum No.35, Mass spectrum, No.32.

(ii) The Adduct (224)

2-(2′-methylprop-1′-enyl)-2-methyl-4,5,6-trisheptafluoroisopropyl-1,3-diaza-2-azaniacyclohexadienide (222) (0.2g, 0.3 mmoles) and carbon tetrachloride (2g) were placed in an n.m.r. tube, in which bromine (1.0g, 6.2 mmoles) was introduced . The solution was heated up to boiling point for *ca.* 5 min. The residue contained one component identifed as 2-(1′,2′-dibromo-2′-methylpropyl)-2-methyl-4,5,6-trisheptaluoroisopropyl-1,3-diaza-2-azania cyclohexadienide (224). A slightly yellow viscous liquid. U.v. spectrum; λ_{max}(ε), 249.2nm (10400), 283nm (6970), 367nm (790). N.m.r. spectra (^{19}F and ^{1}H) No.31. I.r. spectrum No.37. Mass spectrum No.33.

(iii) The Adduct (225)

2-(1´-methylprop-1´-enyl)-1-methyl-4,5,6-trisheptafluoroisopropyl-1,2,3-triazacyclohexa-3,5-diene (223) (0.1g, 0.15 mmoles) and carbontetrachloride (2g) were placed in an n.m.r. tube, in which bromine (1.0g, 6.2 mmoles) was introduced. The solution was heated up to boiling point for *ca.* 5 min. The residue contained a single component identified as 2-(1´,2´-dibromo-1 -methylpropyl)-1-methyl-4,5,6-trisheptafluoroisopropyl-1,2,3-triazacyclohexa-3,5-diene (225). A slightly yellow viscous liquid. N.m.r. spectra (^{19}F and ^{1}H). No.33. I.r. spectrum No.39. Mass spectrum, No.34.

(E) Attempted Solvolysis of (220)

2-(1´,2´-Dimethylprop-1 -enyl)-2-methyl-4,5,6-trisheptafluoroisopropyl-1,3-diaza-2-azaniacyclohexadienide (220) (0.2g, 0.3 mmoles), water (1.0g) and carbontetrachloride (1.0g) were placed in an n.m.r. tube and heated at b.p. for 10 min. The solution (under layer) was shown by ^{1}H n.m.r. spectroscopy to contain unchanged starting material (220).

Then the solution was again heated at b.p. for 10 min. after addition of methanol (1 ml). The starting material (220) remained unchanged.

13.2 2,3-Dimethylbut-1,3-Diene

Perfluorotrisisopropyl-1,2,3-triazine (0.6g,1.02 mmoles) and 2,3-dimethylbut-1,3-diene (2.0g, 24.4 mmoles) were sealed in a Carius tube (20 ml.) under 10^{-2}mm Hg and heated at 70° for 4 days. The product (0.53g) was obtained by vacuum trans-

fer, followed by evaporation of low b.p. materials. Recrystalization from petroleum ether gave brilliant yellow crystals (0.48g, 70%), identified as 6,7,10-trisheptafluoroisopropyl-3,4-dimethyl-1,8,9-triazabicyclo[4,2,2]deca-3,8,9-triene (229) m.p. 85-87°C. [Found: C, 33.7; H, 1.04; F,59.1; N,6.6%: Calculated for $C_{18}H_{10}F_{21}N_3$; C, 32.4; H, 1.5; F, 59.8; N,6.3%]. U.v. spectra: $\lambda_{max}(\varepsilon)$, 195.3nm (10100), 264.7nm (5570), 340.5nm (3400 in acetonitrile; 199.8nm (6620), 263.8nm (5520), 343nm (3640) in cyclohexane. N.m.r. spectra (^{19}F, ^{1}H and ^{13}C). No.34. I.r. spectrum No.40. Mass spectrum No.31. Five unknown minor components were also found in the petrolum ether solution which had the same molecular weight (667).

13.3 Other Attempts

(A) Hard Bases

(i) Methoxide

Perfluorotrisisopropyl-1,2,3-triazine (0.2g, 0.34 m moles) and sodium methoxide/methanol solution (2ml, 0.15M), 0.3 m moles) were mixed in an n.m.r. tube. The dark red coloured tar contained five volatile components, two of which have molecular weights, m/e = 463, ($\{C_3F_7\}_2 \cdot C_3N_3 \cdot O \cdot OCH_3$) and 433 ($\{C_3F_7\}_2 \cdot C_3N_3 \cdot O \cdot H$).

(ii) Triethylamine

The triazine (165) (0.5g, 0.85mmoles) and triethylamine (0.081g, 0.80 mmoles); and dichloromethane 1 ml. were mixed in an n.m.r. tube at room temperature and set aside for 1 day during which time the solution turned to dark red.

The product could not be transferred under high vacuum up to 200°C.

(B) Cycloaddition

(i) Dimethylacetylenedicarboxylate

Perfluorotrisisopropyl-1,2,3-triazine (165)(0.3g, 0.51 mmoles) and dimethylacetylenedicarboxylate (2.0g, excess) were sealed in a Carius tube and heated at 70°C for 5 days. The mixture was shown by ^{19}F n.m.r. spectroscopy to contain unreacted triazine (165).

(ii) Phenylazide

Perfluorotrisisopropyl-1,2,3-triazine (165) (0.3g, 0.51 mmoles) and phenylazide (0.3 g, 2.5mmoles), and ether 5 ml. were placed in a r.b. flask and stirred at room temperature for 5 days. The mixture was shown to contain unreacted triazine (165) by ^{19}F n.m.r. spectroscopy.

(iii) Diazomethane

Perfluorotrisisopropyl-1,2,3-triazine (165) (0.3g, 0.51 mmoles) and diazomethane (5 ml, 2% ether solution) were stirred in a r.b. flask for 5 days. The solution contained unreacted starting material (165).

(C) Perfluoro-4,6-Bisisopropyl-1,2,3-Triazine with Alkenes

(i) 2-Methylbut-2-ene

Perfluoro-4,6-bisisopropyl-1,2,3-triazine (164) (0.22g, 0.5 mmoles) and 2-methylbut-2-ene (2g, 28.6 mmoles)

were sealed in a Carius tube and heated at 70°C for 5 days. the mixture was shown to contain unreacted starting triazine (164).

(ii) 2,3-Dimethylbuta-1,3-diene

Perfluoro-4,6-bisisopropyl-1,2,3-triazine (0.22g, 0.5 mmoles) and 2,3-dimethylbuta-1,3-diene (2.0g, 24.4 m moles) were sealed in a Carius tube under high vacuum and heated at 70°C for 5 days. The mixture contained polymeric product and unreacted the triazine (164) (identified by ^{19}F n.m.r. spectroscopy).

APPENDICES

APPENDIX I

N.M.R. Spectra

1. 4,5-Dichloro-6-fluoro-1,2,3-triazine (161) : (^{19}F).
2. 5-Chloro-4,6-difluoro-1,2,3-triazine (162) : (^{19}F).
3. 4,5,6-Trifluoro-1,2,3-triazine (163) : (^{19}F).
4. Perfluoro-4,6-bisisopropyl-1,2,3-triazine (164) : (^{19}F).
5. Perfluoro-4,5,6-trisisopropyl-1,2,3-triazine (165) : (^{19}F and ^{13}C).
6. Perfluoro-2,4,6-trisisopropyl-5-isopropylidene-1,2,3-triazacyclohexa-3,6-diene (166) : (^{19}F, ^{13}C and ^{15}N).
7. 4,4-Bistrifluoromethyl-6,8,10-trisheptafluoroisopropyl-1,2,7,8,9-pentaazaspiro[4,5]deca-2,6,9-triene (167) : (^{19}F, ^{1}H and ^{13}C).
8. 4,6-Bisheptafluoroisopropyl-2,5-bis(2′-trifluoromethyl-2′-methoxy-3′,3′,3′-trifluoropropyl)-1,2,3-triazacyclohexa-3,6-diene (173) (^{19}F and ^{1}H).
9. 2,4,6-Trisheptafluoroisopropyl-5-(1′,1′-bistrifluoromethyl-acetonyl)-1,2,3-triazacyclohexa-3,6-diene (174) : (^{19}F and ^{1}H).
10. 2-Phenyl-4,6-bisheptafluoroisopropyl-5-heptafluoroisopropylidene-1,2,3-triazacyclohexa-3,6-diene (169) : (^{19}F and ^{1}H).
11. Perfluoro-4,5,6-trisheptafluoroisopropyl-2-(cyclobut-1′-enyl)-1,2,3-triazacyclohexa-3,6-diene (170) : (^{19}F and ^{13}C).
12. Perfluoro-2,4,5-trisisopropylpyrimidine (177) : (^{19}F).
13. Perfluoroisobutyronitrile (46) : (^{19}F).
14. Perfluoro-3-methylbut-1-yne (179) : (^{19}F).
15. 1-Fluoro-2-heptafluoroisopropyl-4-methyl-4-(2′-methyl-prop-2′-enyl)-cyclobut-1-ene (188) : (^{19}F and ^{1}H).
16. 1-Fluoro-2-heptafluoroisopropyl-4,5-dimethyl-cyclohexa-1,4-diene (189) : (^{19}F and ^{1}H).

17. Perfluoro-2,5-dimethylhex-3-yne (45) : (^{19}F).

18. perfluoro-2,5-dimethyl-4-isopropylhexa-2,3-diene (193) : (^{19}F and ^{13}C).

19. Perfluoro-4,5-bisisopropyl-2,8-dimethylocta-2,3,5,6-tetraene (194) : (^{19}F).

20. Perfluoro-6-isopropyl-2,5,5,8-tetramethylnona-6,7-diene-3-yne (195) : (^{19}F).

21. Perfluoro-2,4,6,8-tetrakisisopropyl-1,5-diazatricyclo-[4,2,0,$O^{2,5}$]octa-3,7-diene (180) : (^{19}F).

22. Perfluoro-2,4-bisisopropylpyridine (209) : (^{19}F).

23. (Endo)-1-fluoro-3,4-bisheptafluoroisopropyl-4-aza-9-oxa-tricyclo[4,2,1,$O^{2,5}$]nona-3,7-diene (212) : ^{19}F and ^{1}H).

24. (Endo)-1-fluoro-7,9-bisheptafluoroisopropyl-8-aza-3-oxatricyclo[5,2,0,$O^{2,6}$]nona-4,8-diene (213) : (^{19}F and ^{1}H).

25. (Endo)-9-fluoro-1,8-bisheptafluoroisopropyl-7-aza-3-oxatricyclo[5,2,0,$O^{2,5}$]nona-4,8-diene (214) : (^{19}F and ^{1}H).

26. Perfluoro-2,4,6-trisisopropylpyridine (204) : (^{19}F).

27. Perfluoro-2,4,6,8-tetrakisisopropyl-3,7-diazabicyclo-[4,2,0]octa-2,4,7-triene (206) : (^{19}F).

28. 2-(1',2'-Dimethylprop-1'-enyl)-2-methyl-4,5,6-trishepta-fluoroisopropyl-1,3-diaza-2-azaniacyclohexadidnide (220) : (^{19}F, ^{1}H and ^{13}C).

29. 2-(1',2'-Dimbromo-1',2'-dimethylpropyl)-2-methyl-4,5,6-trisheptafluoroisopropyl-1,3-diaza-2-azaniacyclohexa-dienide (221) ; (^{19}F and ^{1}H).

30. 2-(2'-Methylprop-1'-enyl)-2 -methyl-4,5,6-trisheptafluoro-isopropyl-1,3-diaza-2-azaniacyclohexadienide (222) : (^{19}F, ^{1}H and ^{13}C).

31. 2-(1′,2′-Dimbromo-2′-methylpropyl)-2-methyl-4,5,6-trisheptafluoroisopropyl-1,3-diaza-2-azaniacyclohexadienide (224) : (^{19}F and ^{1}H).

32. 2{1′-Methylprop-1′-enyl}1-methyl-4,5,6-trisheptafluoroisopropyl-1,2,3-triazacyclohexa-3,5-diene (223) : (^{19}F and ^{1}H).

33. 2{1′,2′-Dimbromo-1′-methylpropyl)-1-methyl-4,5,6-trisheptafluoroisopropyl-1,2,3-triazacyclohexa-3,5-diene (225).

34. 6,7,10-Trisheptafluoroisopropyl-3,4-dimethyl-1,8,9-triazabicyclo[4,2,2]deca-3,8,9-triene (229) : (^{19}F, ^{1}H and ^{13}C).

The follow abbreviations are used in this appendix: S, singlet; D, doublet; T, triplet; Q, quartet; H, sextet; Sept, septet; M, multiplet.

Unless otherwise stated spectra were recorded at 40°C in $CDCl_3$.

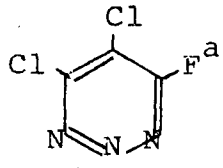
$CFCl_3$, TMS, TMS and $MeNO_2$ were used as reference for ^{19}F, ^{1}H, ^{13}C and ^{15}N spectra respectively.

For ^{1}H and ^{15}N spectra, down field shifts are quoted as positive, whilst for ^{19}F spectra, upfield shifts are quoted as positive.

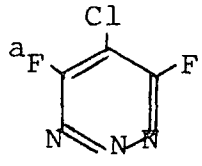
For ^{13}C spectra, "downfield" shifts are quored as positive where downfield is the direction of increasing the absolute values.

Relative intensities in ^{13}C spectra are approximate values.

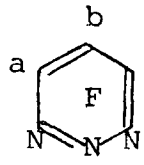
	Shift (p.p.m.)	Fine Structure Coupling Constants (Hz)	Relative Intensity	Assign-ment
1.	4,5-Dichloro-6-fluoro-1,2,3-triazine (161)			
	79.5	S	1	a
2.	5-Chloro-4,6-difluoro-1,2,3-triazine (162)			
	76.7	S	2	a
3.	4,5,6-Trifluoro-1,2,3-triazine (163)			
	95.2	D (J = 22)	2	a
	165.8	T (J = 22)	1	b
4.	Perfluoro-4,6-bisisopropyl-1,2,3-triazine (164)			
	75.5	T (J = 12)	12	c
	124.8	T(J=45.4) of Sept (J=5.6)	1	a
	186.3	D(J=45.4) of Sept (J=5.6)	2	b



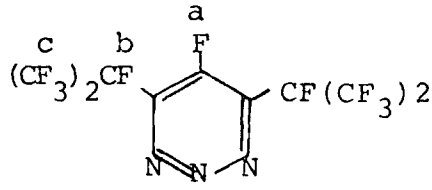
(161)



(162)



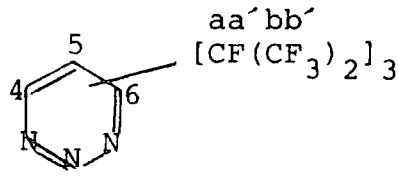
(163)



(164)

5.	Perfluoro-4,5,6-trisisopropyl-1,2,3-triazine (165)			
	^{19}F spectrum (neat)			
	72.4	D (J = 39)	6	5b´
	74.5	D(J=17.5) of D(J=3.9)	6	4b´
	75.3	S	6	6b´
	154.7	D(J=117) of Sept (J=4.0)	1	5a´
	180.3	D(J=117) of Sept !J=3.9)	1	4a´
	184.6	Sept (J = 39)	1	6a´

Shift (p.p.m.)	Fine Structure Coupling Constants (Hz)	Relative Intensity	Assign-ment
5. (continued)			
^{13}C spectrum (solvent; $(CD)_3C=O$)			
148.1	D (J = 27.9)	1	6
145.5	D(J=29.3) of D(J=2.8)	1	4
119.0	Q(J=288.3) of D(J=27.8)	4	4b, 6b
118.9	Q(J=289.2) of D(J=26.5)	2	5b
118.0	D (J = 30.3)	1	5
93.8	D(J=175.4) of Sept (J=36.5)	1	5a
92.8	D(J=217.0) of Sept (J=34.0)	2	4a, 6a

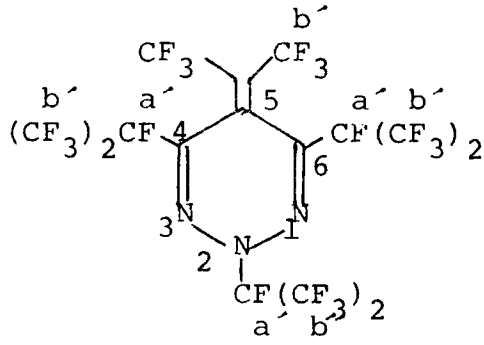


(165)

6. Perfluoro-2,4,6-trisisopropyl-5-isopropylidene-1,2,3-triazacyclohexa-3,6-diene (166)

^{19}F spectra: at 40°C (neat)			
61.3	D (J = 39.5)	6	5b'
72.9	S	6	4b' or 6b'
77.7	S	6	2b'
78.2	S	6	6b' or 4b'
153.4	S	1	2a'
177.6	Q (J = 39.5)	2	4a' and 6a'
: above 75°C (neat)			
61.4	D (J = 39.5)	6	5b'
75.4	S	12	4b' and 6b'
77.9	S	6	2b'
153.0	S	1	2a'

Shift (p.p.m.)	Fine Structure Coupling Constants (Hz)	Relative Intensity	Assign-ment
6. (continued)			
176.7	Q (J = 39.5)	2	4a and 6a



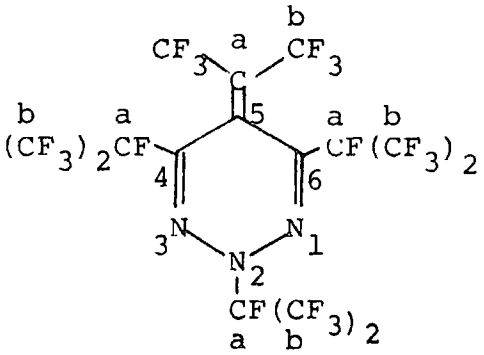
(166)

^{13}C spectrum (solvent: $(CD_3)_2C=O$)

125.5	D (J = 36.9)	2	4 and 6
122.3	Sept (J = 34.2)	1	5a
118.9	Q(J=288.4) of D(J=26.1)	4	4b and 6b
118.86	Q (J = 279.2)	2	5b
118.2	Q(J=289.3) of D(J=29.4)	2	2b
117.8	S	1	5
97.2	D(J=236.2) of Sept(J=35.9)	1	2a
92.9	D(J=216.6) of Sept(J=35.4)	2	4a and 6a

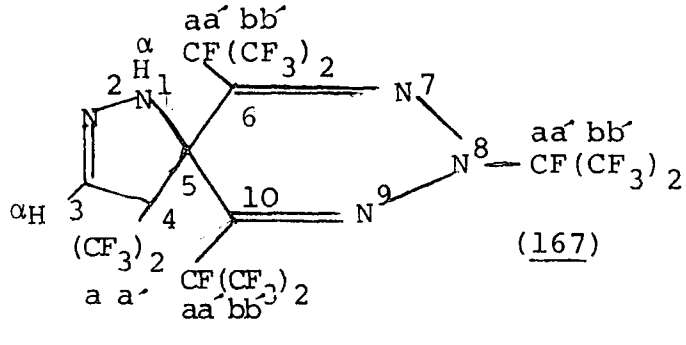
^{15}N spectrum (solvent: $CF_2ClCFCl_2/(CD_3)_2C=O$)

-46.4	S	2	1 and 3
+40.2	D (J = 14)	1	2



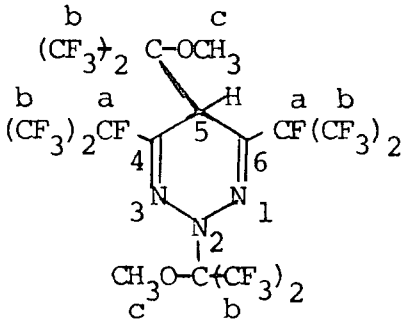
(166)

Shift (p.p.m.)	Fine Structure Coupling Constant (Hz)	Relative Intensity	Assign-ment
7.	4,4-Bistrifluoromethyl-6,8,10-trisheptafluoroisopropyl-1,2,7,8,9-pentaazaspiro[4,5]deca-2,6,9-triene (167)		
	^{19}F spectrum		
65.7	D (J = 11.3)	6	4a´
72.7	T (J = 4.7)	6	6b´or 10b´
75.5	T (J = 4.7)	6	10b´or 6b´
77.1	S	6	8b´
153.4	S	1	8a´
184.3	S broad	2	6a´and 10a´
	^{13}C spectrum (solvent: $(CD_3)_2C=O$)		
126.1	S	(1)	3
125.8	D (J = 30)	2	6 and 10
120.3	Q (J = 284.7)	2	4a
119.1	Q(J=289.1) of D(J=25.9)	2	8b
118.9	Q(J=288.2) of D(J=29.1)	2	6b or 10b
118.1	Q(J=289.6) of D(J=29.7)	2	10b or 6b
96.2	D(J=235.1) of Sept(J=35.5)	1	8a
92.9	D(J=223.2) of Sept(J=33.1)	2	6a and 10a
76.2	Sept (J = 27.7)	1	4
63.3	S	1	5
	^{1}H spectrum (solvent: $(CD_3)_2C=O$)		
7.2	S	1	3α
8.4	S broad	1	1α

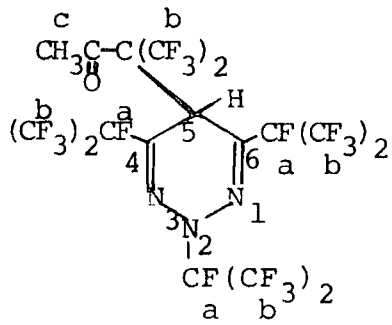


(167)

Shift (p.p.m.)	Fine Structure Coupling Constant (Hz)	Relative Intensity	Assign-ment
8. 4,6-Bisheptafluoroisopropyl-2,5-bis(2´-trifluoromethyl-2´-methoxy-3´,3´,3´-trifluoropropyl)-1,2,3-triazacyclohexa-3,6-diene (173)			
^{13}F spectrum			
67.8	T (J = 14.8)	6	5b
73.1	S	12	4b and 6b
78.1	S sharp	6	2b
181.1	S broad	2	4a and 6a
^{1}H spectrum			
3.6	S	6	5c and 2c
4.7	S	1	5



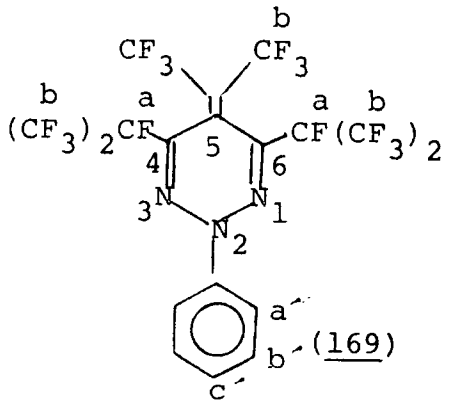
(173)



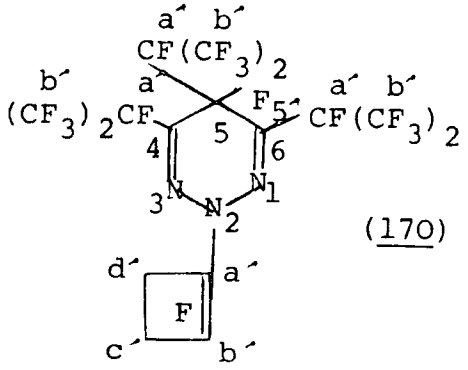
(174)

9. 2,4,6-Trisheptafluoroisopropyl-5-(1´,1´-bistrifluoromethyl-acetonyl)-1,2,3-triazacyclohexa-3,6-diene (174)			
63.3	T (J = 6.7)	6	5b
73.0	S	6	4b or 6b
76.3	S sharp	6	2b
77.3	S	6	6b or 4b
154.2	S	1	2a
181.2	S broad	2	4a and 6a

Shift (p.p.m.)	Fine Structure (Coupling Constant (Hz)	Relative Intensity	Assign-ment
9. (continued)			
^{1}H spectrum			
2.47	S	3	5c
5.1	S	1	5
10. 2-Phenyl-4,6-bisheptafluoroisopropyl-5-heptafluoroisopropylidene-1,2,3-triazacyclohexa-3,6-diene (169)			
60.3	D (J = 37)	6	5b
75.0	S	12	4b and 6b
177.3	Q (J = 37)	2	4a and 6a
^{1}H spectrum			
7.6 - 8.3	M	5	2a´,b´,c´



(169)



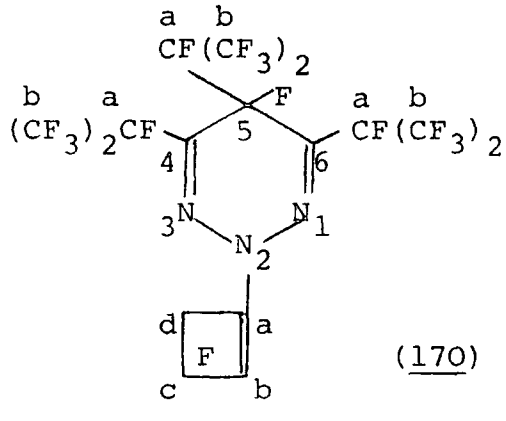
(170)

11. Perfluoro-4,5,6-trisheptafluoroisopropyl-2-(cyclobut-1-enyl)-1,2,3-triazacyclohexa-3,6-diene (170)

^{19}F spectrum (solvent: Et_2O)

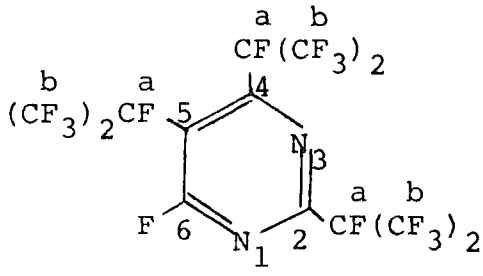
74.0	S	6	4b´ or 6b´
74.5	S	6	5b´
77.3	S	6	6b´ or 4b´

Shift (p.p.m.)	Fine Structure Coupling Constant (Hz)	Relative Intensity	Assign-ment
11. (continued)			
119.6	M	2	2c′ or 2d′
120.4	M	2	2d′ or 2c′
126.7	M	1	2b′
151.7	S broad	1	5a′
179.7	S broad	1	5′
188.7	S broad	2	4a′ and 6a′
^{13}C spectrum			
138.0	D(J=341) of T(J=20.6) of T(J = 6.4	1	2b
124.4	D(J = 32.2) of D(J=22.6)	2	4 and 6
119.1	Q(J=288.4) of D(J=25.8)	2	4b or 6b
118.7	Q(J=288.6) of D(J=27.8)	2	5b
118.4	Q(J=288.8) of D(J=25.8)	2	6b or 4b
116-109	Complex	3	2a,2c,2d
92.5	D(J=219.1) of Sept(J=33.1)	1	5a
91.6	D(J=217.6) of Sept(J=34.2)	2	4a and 6a
79.3	D(J=225.5) of Sept(J=28.3)	1	5

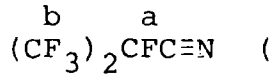


(170)

Shift (p.p.m.)	Fine Structure Coupling Constant (Hz)	Relative Intensity	Assign-ment
12. Perfluoro-2,4,5-trisisopropylpyrimidine (177)			
61.7	S	1	6
75.5	D (J = 3.7)	6	4b
77.6	T (J = 7.4)	6	5b
78.9	Sept (J = 28)	6	2b
159.0	M	1	5a
184.3	M	1	2a or 4a
188.5	M	1	4a or 2a



(177)



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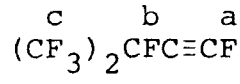

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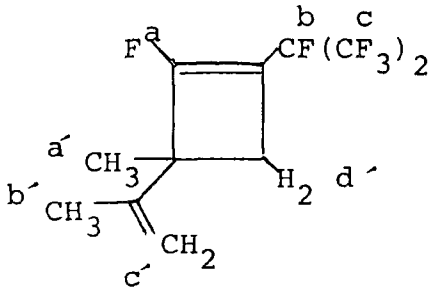
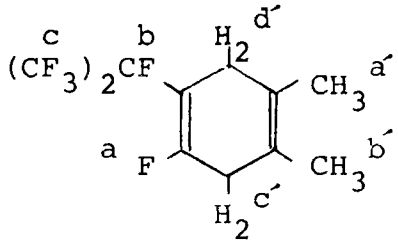
13. Perfluoroisobutyronitrile (46)			
76.4	D (J = 10)	6	b
176.9	H (J = 10)	1	a
14. Perfluoro-3-methylbut-1-yne (179)			
78.2	D (J = 10)	6	c
170.0	Sept (J = 10.0)	1	b
192.7	D (J = 7.5)	1	a

Shift (p.p.m.)	Fine Structure Coupling Constant (Hz)	Relative Intensity	Assign-ment
15. 1-Fluoro-2-heptafluoroisopropyl-4-methyl-4-(2´-methyl-prop-2´-enyl)-cyclobut-1-ene (188)			
^{19}F spectrum			
77.2	T (J = 7.1)	6	c
86.0	M	1	a
184.8	S broad	1	b
^{1}H spectrum			
1.93	S	6	a´, b´
3.28	D (J = 12)	2	d´
5.10	S	2	c´



(188)



(189)

16. 1-Fluoro-2-heptafluoroisopropyl-4,5-dimethyl-cyclohexa-1,4-diene (189)

^{19}F spectrum

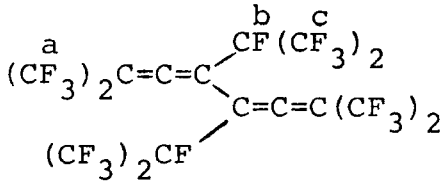
76.3	D (J=17) of D(J=6.5)	6	c
93.0	M	1	a
181.4	S broad	1	b

	Shift (p.p.m.)	Fine Structure Coupling Constant (Hz)	Relative Intensity	Assignment
16.	(continued)			
	^{1}H spectrum			
	1.65	S	6	a and b
	2.83	D (J = 3.7)	2	d
	2.90	S	2	c
17.	Perfluoro-2,5-dimethylhex-3-yne (45)			
	80.1	D (J = 10)	6	b
	175.6	H (J = 10)	1	a

$$\underset{(45)}{(\overset{b}{CF_3})_2\overset{a}{C}FC{\equiv}CCF(CF_3)_2} \qquad \underset{(193)}{\{(\overset{6}{CF_3})_2\overset{5}{\underset{a}{C}}F\}_2\overset{4}{C} = \overset{3}{C} = \overset{2}{C}\overset{1}{(CF_3)_2}}$$

18.	Perfluoro-2,5-dimethyl-4-isopropylhexa-2,3-diene (193)			
	^{19}F spectrum			
	64.3	S	6	1a
	77.7	S	12	6a
	184.0	S	2	5a
	^{13}C spectrum			
	202.9	S	1	3
	118.1	Q(J=287.4) of T(J=12.8)	4	6
	117.6	Q(J = 275.8)	2	1
	104.7	Sept (J = 40)	1	2
	97.5	T (J = 26.9)	1	4
	88.9	D(J=224.0) of Sept(J=34.4)	2	5
19.	Perfluoro-4,5-bisisopropyl-2,8-dimethylocta-2,3,5,6-tetraene (194)			
	64.3	S	12	a
	79.3	S	12	c

Shift (p.p.m.)	Fine Structure Coupling Constant (Hz)	Relative Intensity	Assignment
19. (continued)			
181.5	S	2	b



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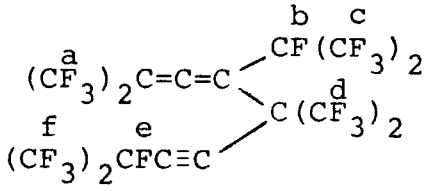


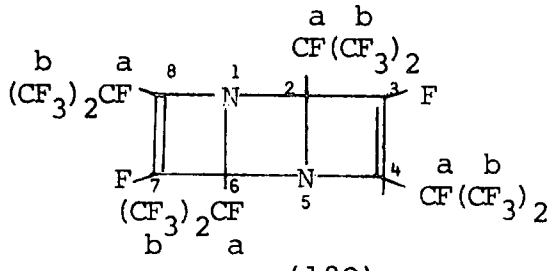
(195)

20. Perfluoro-6-isopropyl-2,5,5,8-tetramethylnona-6,7-diene-3-yne (195)

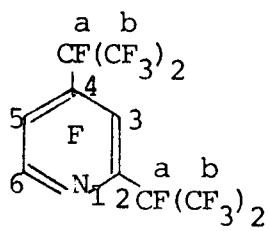
64.3	S	6	a
70.7	D (J = 5.6)	6	d
78.5	D (J = 5.6)	6	b
80.3	D (J = 9.6)	6	f
174.7	M	1	e
180.5	M	1	b

21. Perfluoro-2,4,6,8-tetrakisisopropyl-1,5-diazatricyclo-[4,2,0,$O^{2,5}$]octa-3,7-diene (180)

76.4	S	6	4b or 8b
77.2	S	12	2b and 6b
77.6	S	6	8b or 4b
112.4	D (J = 56.2)	1	3 and 7
113.0	D (J = 56.2)	1	
185.5	M (J = 5.6)	2	2a and 6a
185.8	D(J=56.2) of Sept (J=5.6)	2	4a and 8a



(180)



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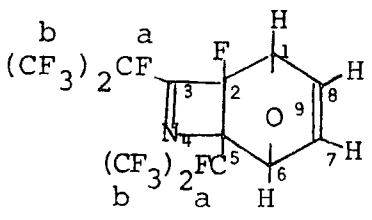
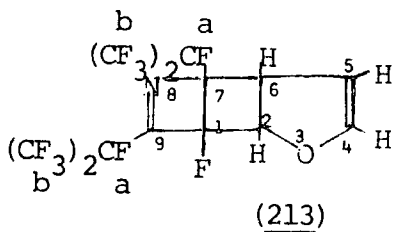
Shift (p.p.m.)	Fine Structure Coupling Constant (Hz)	Relative Intensity	Assign-ment
22. Perfluoro-2,4-bisisopropylpyridine (209)			
76-78	M	12	2b and 4b
85.0	T (J = 59)	1	6
115.0	M	1	3
124.7	M	1	5
181.0	T (J = 45)	1	4a
186.0	T (J = 59)	1	2a
23. (Endo)-2-fluoro-3,4-bisheptafluoroisopropyl-4-aza-9-oxatricyclo[4,2,1,$O^{2,5}$]nona-3,7-diene (212)			
^{19}F spectrum			
73.5	T (J = 6.9)	6	3b
75.2	D (J = 9.0)	6	5b
150.0	S	1	2
186.4	Sept (J = 6.9)	2	3a and 5a
^{1}H spectrum			
5.53	S	1	1
5.70	M	1	6
6.87	S	2	7 and 8



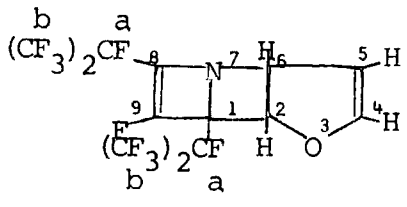
(212)



(213)

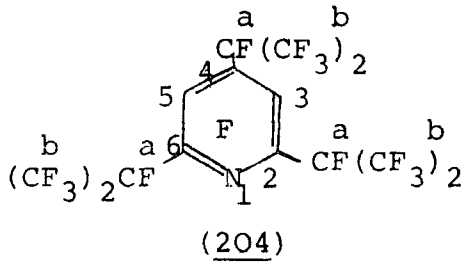
24. (Endo)-1-fluoro-7,9-bisheptafluoroisopropyl-8-aza-3-oxatricyclo[5,2,0,$O^{2,6}$]nona-4,8-diene (213)			
^{19}F spectrum			
73.9	D (J = 9.0)	6	7b
76.4	S	6	9b

	Shift (p.p.m.)	Fine Structure Coupling Constants (Hz)	Relative Intensity	Assignment
24.	(continued)			
	150.0	S	1	1
	186.7	S	2	7a and 9a
	^{1}H spectrum			
	4.3 - 4.7	Complex	2	5 and 6
	5.8	S	1	2 and 4
	6.0	S	1	2 and 4
25.	(Endo)-9-fluoro-1,8-bisheptafluoroisopropyl-7-aza-3-oxa-tricyclo[5,2,0,$O^{2,5}$]nona-4,8-diene (214)			
	^{19}F spectrum			
	78.4	S	6	7b
	79.8	D (J = 56)	6	1b
	97.3	D (J = 65)	1	9
	186.0	D (J = 65)	1	8a
	187.3	S	1	1a
	^{1}H spectrum			
	5.6	D (J = 13)	1	5 and 6
	5.8	Broad	1	5 and 6
	6.0	S	1	2 and 4
	6.3	S	1	2 and 4

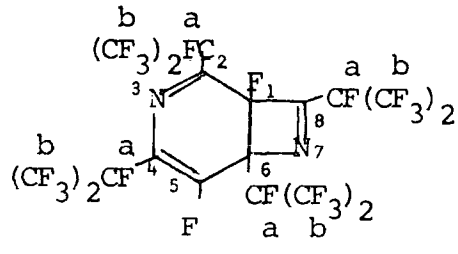


(214)

Shift (p.p.m.)	Fine Structure (Ccupling Constant (Hz)	Relative Intensity	Assign-ment
26. Perfluoro-2,4,6-trisisopropylpyridine (204)			
77.7	S	12	2b and 6b
79.2	T (J = 20)	6	4b
107.2	Broad	2	3 and 5
181.8	D(J=97.3) of Sept (J=5.6)		4a
187.9	D(J=60) of Sept (J=5.6)		2a and 6a



(204)



(206)

27. Perfluoro-2,4,6,8-tetrakisisopropyl-3,7-diazabicyclo-[4,2,0]octa-2,4,7-triene (206)

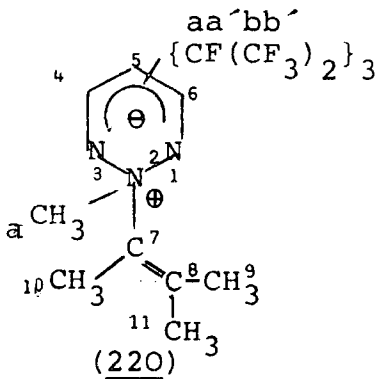
76 - 78	Complex	24	2b,4b,6b,8b
105.3	D broad (J=74)	1	5
161.7	S broad	1	1
182.0	S broad	2	2a, 4a, 6a and 8a
187.0	S broad	1	
189.0	S broad	1	

28. 2-(1',2'-dimethylprop-1'-enyl)-2-methyl-4,5,6-trisheptafluoro-isopropyl-1,3-diaza-2-azaniacyclohexadienide (220)

^{19}F spectrum (neat)

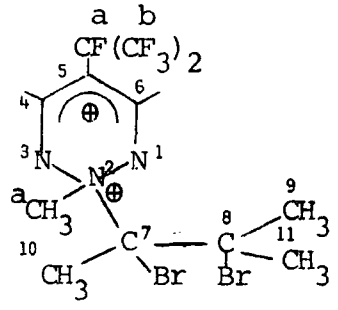
73.7	S	6	4b' or 6b'
75.9	S	6	5b'
78.0	S	6	6b' or 4b'

	Shift (p.p.m.)	Fine Structure Coupling Constants (Hz)	Relative Intensity	Assign-ment
28.	(continued)			
	177.9	S	1	5a
	182.0	S	2	4a and 6a
	^{1}H spectrum (neat)			
	1.47	S	9	9´,10´,11´
	4.82	S	3	2a´
	^{13}C spectrum (neat)			
	152.3	S	1	8
	125.8	Q (J=292.7) of M	(6)	4b,5b,6b
	123.6	D (J = 37)	>1	4 and 6
	118.1	S	1	7
	95.7-98.4	Q of Sept (overlapped)	(3)	4a,5a,6a
	78.1	S	1	2a
	37.2	D (J = 25)	1	5
	30.4	S	≥2	10, 11
	23.2	S	1	9



(220)

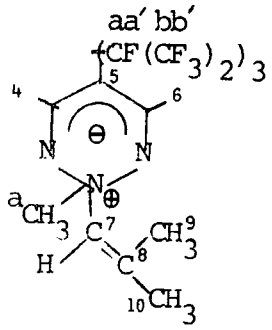
Shift (p.p.m.)	Fine Structure Coupling Constant (Hz)	Relative Intensity	Assign-ment
29. 2-(1′,2′-Dibromo-1′,2′-dimethylpropyl)-2-methyl-4,5,6-trisheptafluoroisopropyl-1,3-diaza-2-azaniacyclohexadienide (221)			
^{19}F spectrum (solvent: $CDCl_3$)			
73.4	S	6	4b or 6b
75.6	D (J = 5.6)	6	5b
77.2	D (J = 5.6)	6	6b or 4b
177.7	S	1	5a
181.0	S	2	4a, 6a
^{1}H spectrum			
1.70	S	3	10
1.80	S	6	9, 11
3.90	S	3	2a



(221)

30. 2-(2′-methylprop-1′-enyl)-2-methyl-4,5,6-trisheptafluoroisopropyl-1,3-diaza-2-azaniacyclohexadienide (222)			
^{19}F spectrum			
73.4	S	6	4b′ or 6b′
75.7	S	6	5b′
77.9	S	6	6b′ or 4b′
177.6	S	1	5a′
181.5	S	2	4a′ and 6a′

	Shift (p.p.m.)	Fine Structure Coupling Constants (Hz)	Relative Intensity	Assign-ment
30.	(continued)			
	^{1}H spectrum			
	1.57	S broad	6	9′, 10′
	4.56 (sh)	M	1	7′
	4.80	S broad	3	2a′
	^{13}C spectrum			
	148.0	S	1	8
	125.0	Q(J=283.4) of M	(6)	4b,5b,6b
	123.0	D (J = 37)	>1	4 and 6
	119.7	S	1	7
	94 - 97.4	Q of Sept (overlapped)	(3)	4a,5a,6a
	76.2	S	1	2a
	36.6	D (J = 25)	1	5
	23.1	S	1	9
	21.4	S	1	10



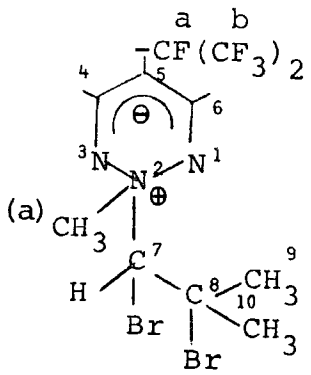
(222)

31. 2-(1′,2′- Dibromo-2′-methylpropyl)-2-methyl-4,5,6-trisheptafluoroisopropyl-1,3-diaza-2-azaniacyclohexadienide (224)

^{19}F spectrum

73.4	S	6	4b or 6b
75.6	S	6	5b
77.8	S	6	6b or 4b
177.6	S	1	5a
181.3	S	2	4a, 6a

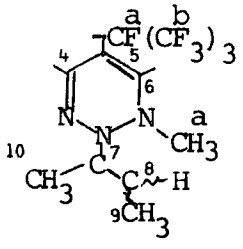
Shift (p.p.m.)	Fine Structure Coupling Constant (Hz)	Relative Intensity	Assignment
31. (continued)			
^{1}H spectrum			
1.86	S broad	6	9, 10
3.9	S	3	2a
6.2	Broad	1	7



(224)

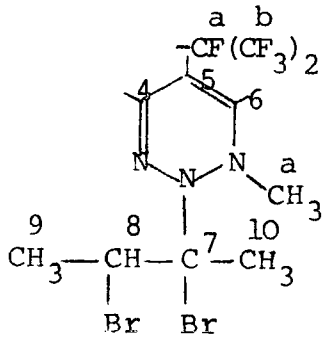
32. 2-(1′-methylprop-1′-enyl)-1-methyl-4,5,6-trisheptafluoroisopropyl-1,2,3-triazacyclohexa-3,5-diene (223)

^{19}F spectrum (solvent: CCl_4)			
71	S	3	4b, 5b and 6b
73-74	M	15	
160.0	D (J = 160)	1	5a
174.4	Q (orT) (J=46)	1	6a
174.8	D(J = 160)	1	4a
^{1}H spectrum			
0.93	D (J = 5)	3	9
1.73	S	3	10
4.10	M (J = 5)	1	8
4.8	S	3	1a



(223)

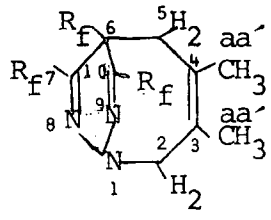
Shift (p.p.m.)	Fine Structure Coupling Constant (Hz)	Relative Intensity	Assignment
33. 2-(1´,2´-Dibromo-1´-methylpropyl)-1-methyl-4,5,6-heptafluoroisopropyl-1,2,3-triazacyclohexa-3,5-diene (225)			
^{19}F spectrum (solvent: CCl_4)			
70.3	S	3)	4b,5b,6b
72.9	M	15)	
159.6	D(J = 157)	1	5a
173.8	Q(or T) (J=46)	1	6a
173.9	D (J = 157)	1	4a
^{1}H spectrum			
1.03	broad	3	10
1.93	D broad (J=9.3 Hz)	3	9
3.80	broad	3	1a
5.70	broad	1	8



(225)

34. 6,7,10-Trisheptafluoroisopropyl-3,4-dimethyl-1,8,9-triazabicyclo[4,2,2]deca-3,8,9-triene (229)			
^{19}F spectrum			
73.3	S	6)	7b´ and 10b´
75.8	S	6)	
73-76	Broad	6	6b´
152.3	S broad	1	6a´
181.0	S broad	2	7a´ and 10a´

Shift (p.p.m.)	Fine Structure Coupling Constant (Hz)	Relative Intensity	Assign-men
34. (continued)			
^{1}H spectrum			
1.80	S	6	3a′ and 4a′
4.28	S	2	2′
4.83	S	2	5′
^{13}C spectrum			
155.9	D broad	(2)	7 and 10
12	S	1	3
12	S	1	4
121.1	Q(J=288.8) of D(J=29.2)	(2)	6b
119.9	Q(J=287.5) of D(J=27.3)	(4)	7b and 10b
94.7	D(J=218.2) of Sept(J=35.0)	(1)	6a
93.4	D(J = 54.1)	(1)	6
91.4	D(J=245.0) of Sept(J=33.8)	(2)	7a and 10a
83.7	S	1	2
74.0	S	1	5
11.1	S	1	3a
10.8	S	1	4a



aabb′
[R_f = CFCF$_3$]

APPENDIX II

I.R. Spectra

1. 4,5,6-Trichloro-1,2,3-triazine (157).
2. 5-Chloro-4,6-difluoro-1,2,3-triazine (162).
3. 4,5,6-Trifluoro-1,2,3-triazine (163).
4. Perfluoro-4,6-bisisopropyl-1,2,3-triazine (164).
5. Perfluoro-4,5,6-trisisopropyl-1,2,3-triazine (165).
6. Perfluoro-2,4,6-trisisopropyl-5-isopropylidene-1,2,3-triazacyclohexa-3,6-diene (166).
7. 4,4-Bistrifluoromethyl-6,8,10-trisheptafluoroisopropyl-1,2,7,8,9-pentaazaspiro[4,5]deca-2,6,9-triene (167).
8. 4,6-Bisheptafluoroisopropyl-2,5-bis(2′-trifluoromethyl-2′-methoxy-3′,3′,3′-trifluoropropyl)-1,2,3-triazacyclohexa-3,6-diene (173).
9. 2,4,6-Trisheptafluoroisopropyl-5-(1′,1′-bistrifluoromethyl-acetonyl)-1,2,3-triazacyclohexa-3,6-diene (174).
10. 2-Phenyl-4,6-bisheptafluoroisopropyl-5-heptafluoroisopropyl-idene-1,2,3-triazacyclohexa-3,6-diene (169).
11. Perfluoro-4,5,6-trisheptafluoroisopropyl-2-(cyclobut-1′-enyl)-1,2,3-triazacyclohexa-3,6-diene (170).
12. Trichloroacrylonitrile (34).
13. Perfluoro-2,4,5-trisisopropylpyrimidine (177).
14. Perfluoroisobutyronitrile (46).
15. 50/50 mixture of perfluoro-3-methylbut-1-yne (179) and perfluoroisobutyronitrile (46).
16. 1-Fluoro-2-heptafluoroisopropyl-4-methyl-4-(2′-methyl-prop-2′-enyl)-cyclobut-1-ene (188).
17. 1-Fluoro-2-heptafluoroisopropyl-4,5-dimethyl-cyclohexa-1,4-diene (189).

18. 50/50 mixture of Perfluoro-2,5-dimethylhex-3-yne (45) and perfluoroisobutyronitrile (46).
19. Perfluoro-2,5-dimethyl-4-isopropylhexa-2,3-diene (193).
20. 50/50 mixture of perfluoro-4,5-bisisopropyl-2,8-dimethyl-octa-2,3,5,6-tetraene (194) and perfluoro-6-isopropyl-2,5,5,8-tetramethylnona-6,7-diene-3-yne (195).
21. Poly(trifluoroazete) (201).
22. Poly(trifluoroazete-co-hexafluorobut-2-yne) (202).
23. Perfluoro-2,4,6,8-tetrakisisopropyl-1,5-diazatricyclo-[4,2,0,$O^{2,5}$]octa-3,7-diene (180).
24. Perfluoro-2,4-bisisopropylpyridine (209).
25. 60/40 mixture of (endo)-2-fluoro-3,4-bisheptafluoroisopropyl-4-aza-9-oxatricyclo[4,2,1,$O^{2,5}$]nona-3,7-diene (212) and (endo)-1-fluoro-7,9-bisheptafluoroisopropyl-8-aza-3-oxatricyclo[5,2,0,$O^{2,6}$]nona-4,8-diene (213).
26. 9-Fluoro-1,8-bisheptafluoroisopropyl-7-aza-3oxatricyclo-[5,2,0,$O^{2,5}$]nona-4,8-diene (214).
27. Perfluoro-2,4,6-trisisopropylpyridine (204).
28. Photolysate from 4,5,6-trifluoro-1,2,3-triazine at 77K, *i.e.*, trifluoroazete (175) (with minor components).
29. 4,5,6-Trifluoro-1,2,3-triazine at 77K.
30. Photolysate from perfluoro-4,6-bisisopropyl-1,2,3-triazine at 77K.
31. Perfluoro-2,4,6,8-tetrakisisopropyl-1,5-diazatricyclo-[4,2,0,$O^{2,5}$]octa-3,7-diene (180) at 77K.
32. A mixture of perfluoro-2,4,6-8-tetrakisisopropyl-3,7-diazabicyclo[4,2,0]octa-2,4,7-triene (206) and perfluoro-2,4,6,8-tetrakisisopropyl-1,5-diazatricyclo[4,2,0,$O^{2,5}$]-octa-3,7-diene (180) and (217).

33. Photolysate from perfluoro-4,5,6-trisisopropyl-1,2,3-triazine, *i.e.*, 50/50 mixture of perfluoroisobutyronitrile (46) and perfluoro-2,5-dimethylhex-3-yne (45), at 77K.

34. 2{1′,2′-Dimethylprop-1′-enyl}2-methyl-4,5,6-trisheptafluoroisopropyl-1,3-diaza-2-azaniacyclohexadienide (220).

35. 2-(1′,2′-Dibromo-1′,2′-dimethylpropyl)-2-methyl-4,5,6-trisheptafluoroisopropyl-1,3-diaza-2-azaniacyclohexadienide (221).

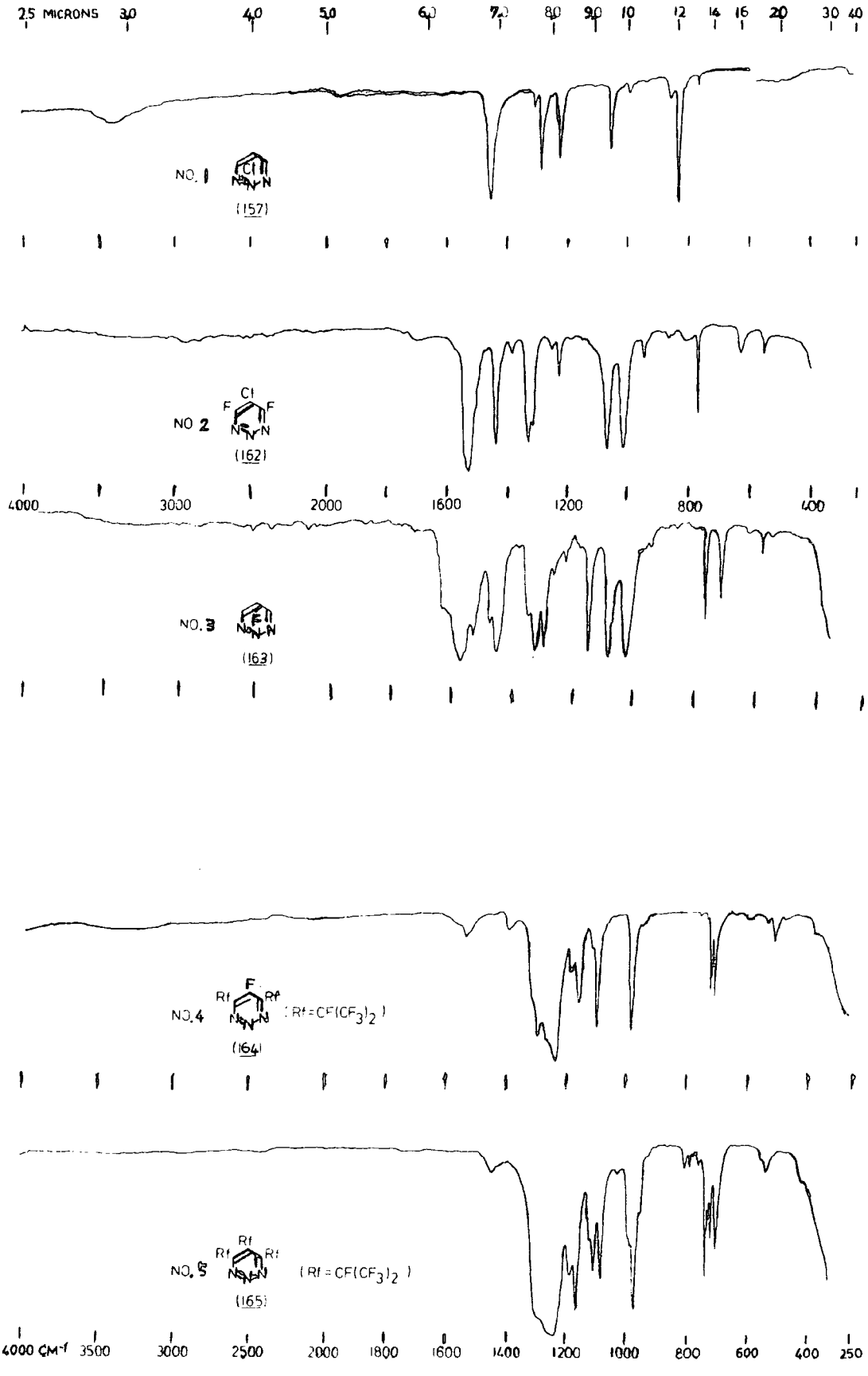
36. 2{2′-Methylprop-1′-enyl}2-methyl-4,5,6-trisheptafluoroisopropyl-1,3-diaza-2-azaniacyclohexadienide (222).

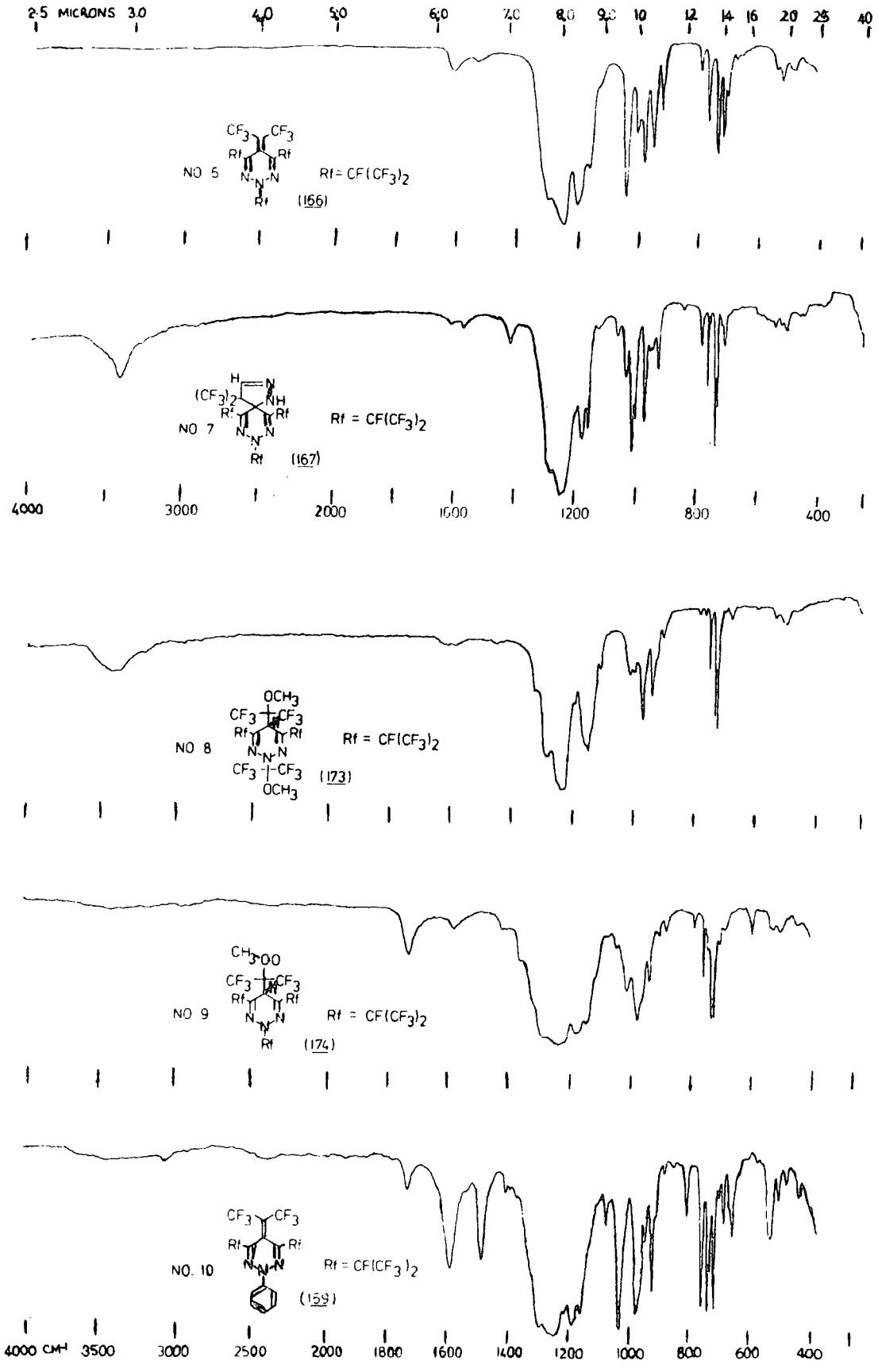
37. 2-(1′,2′-Dibromo-2′-methylpropyl)-2-methyl-4,5,6-trisheptafluoroisopropyl-1,3-diaza-2-azaniacyclohexadienide (224).

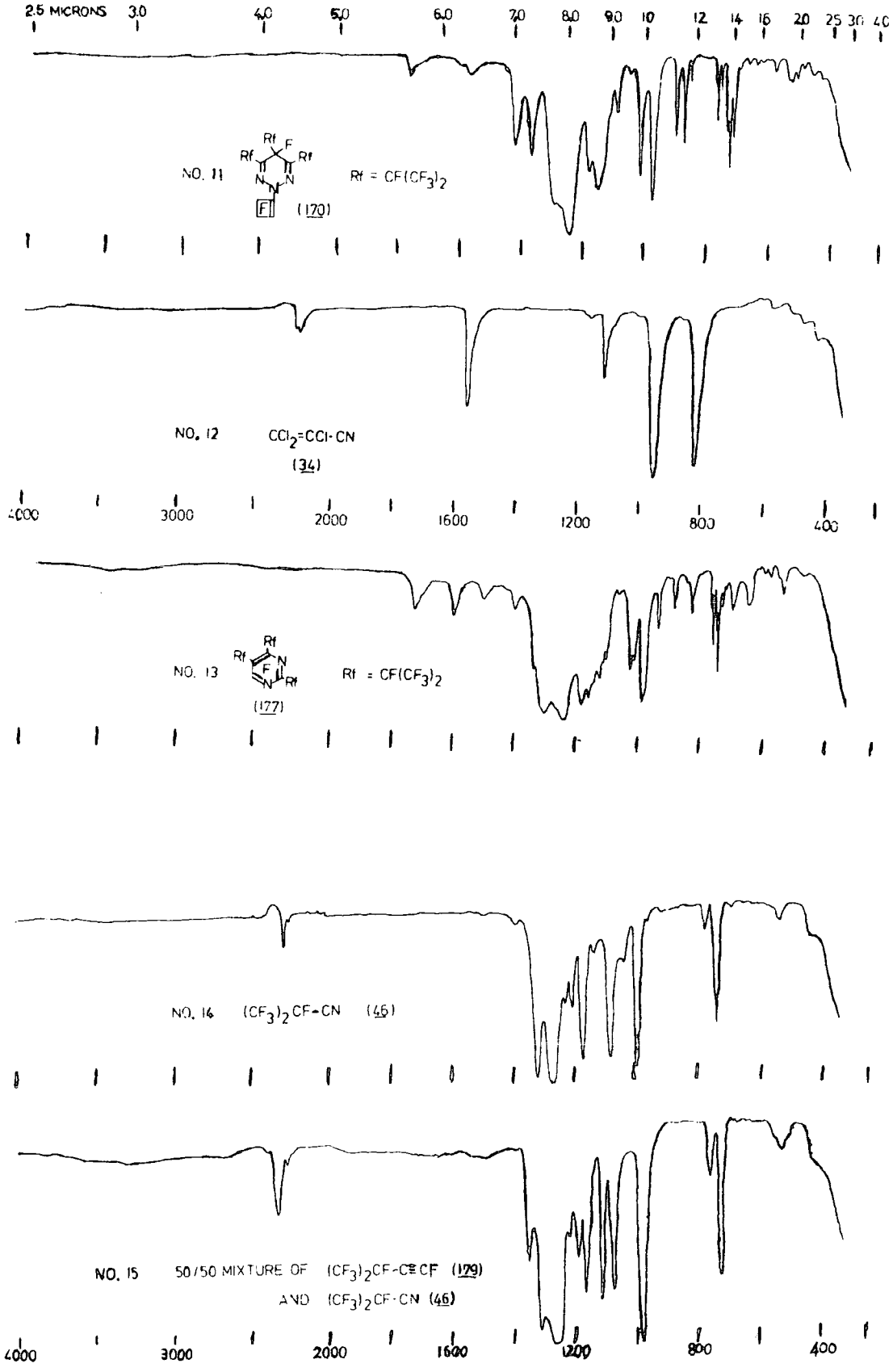
38. 2{1′-Methylprop-1′-enyl}1-methyl-4,5,6-trisheptafluoroisopropyl-1,2,3-triazacyclohexa-3,5-diene (223).

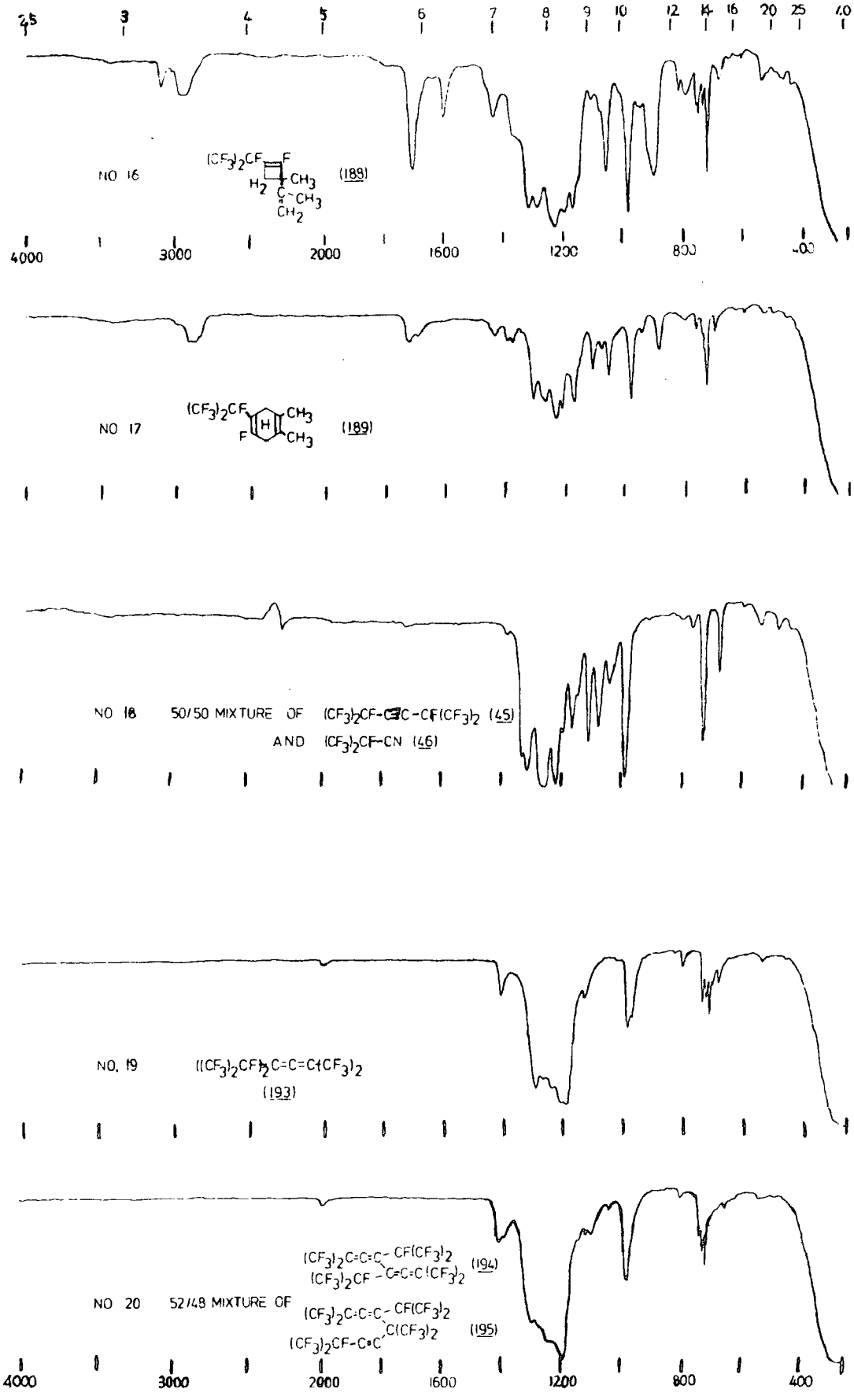
39. 2-(1′,2′-Dibromo-1′-methylpropyl)-1-methyl-4,5,6-trisheptafluoroisopropyl-1,2,3-triazacyclohexa-3,5-diene (225).

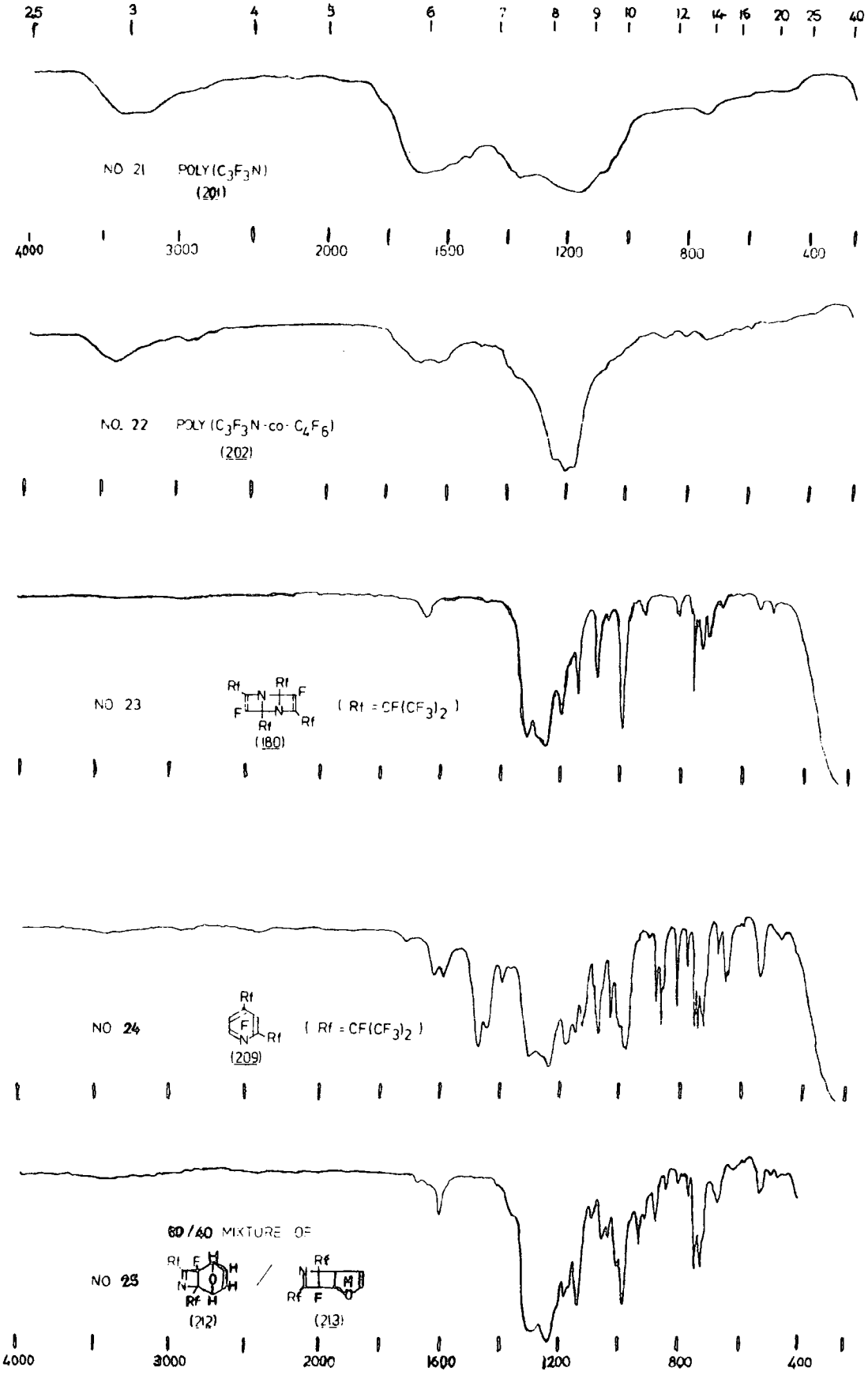
40. 6,7,10-Trisheptafluoroisopropyl-3,4-dimethyl-1,8,9-triaza bicyclo[4,2,2]deca-3,8,9-triene (229).

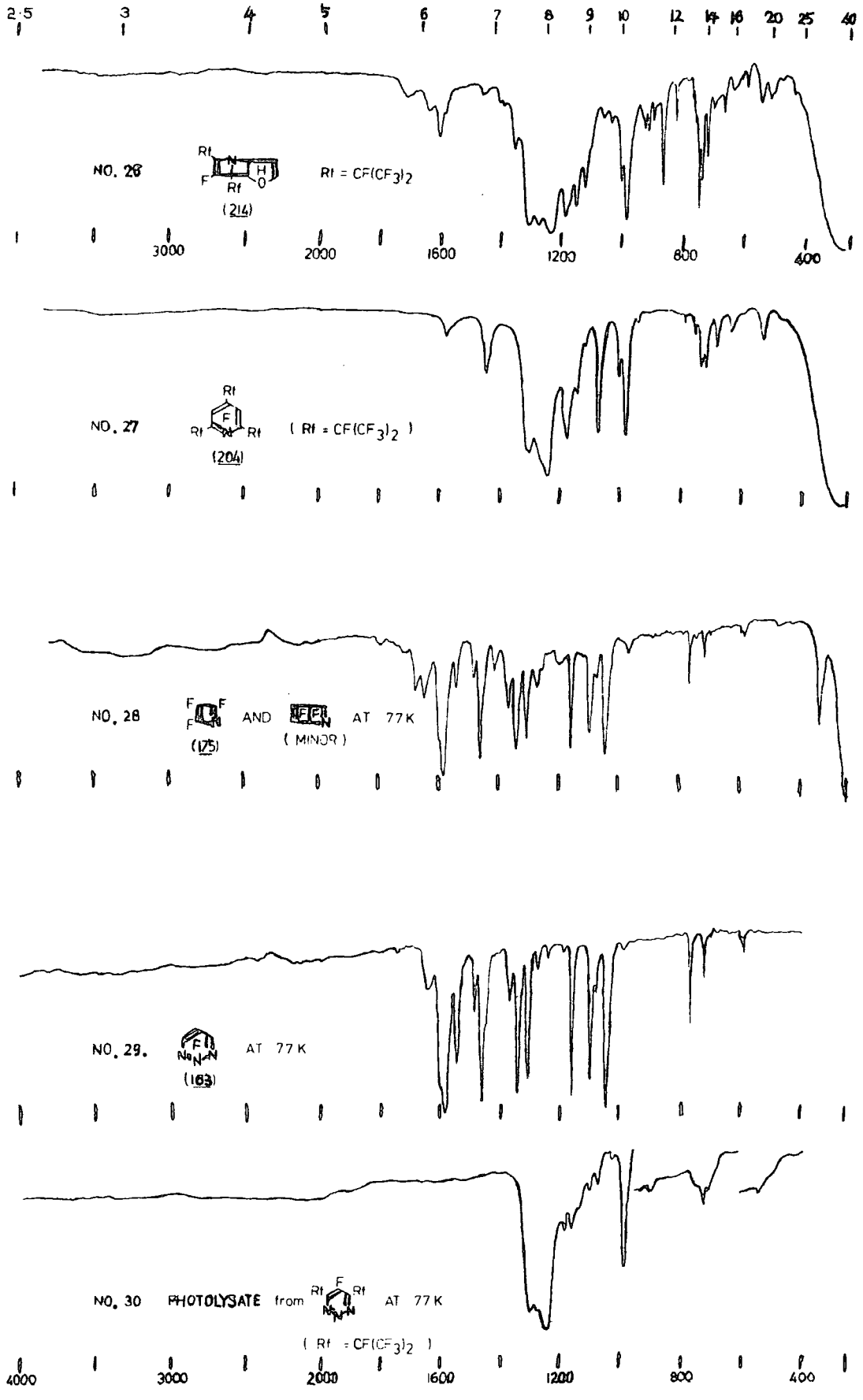

2.5 MICRONS 3.0 4.0 5.0 6.0 7.0 8.0 9.0 10 12 14 16 20 30 40
NO. 1
(157)
NO. 2
(162)
4000 3000 2000 1600 1200 800 400
NO. 3
(163)
NO. 4
(164)
NO. 5
(165)
4000 CM-1 3500 3000 2500 2000 1800 1600 1400 1200 1000 800 600 400 250

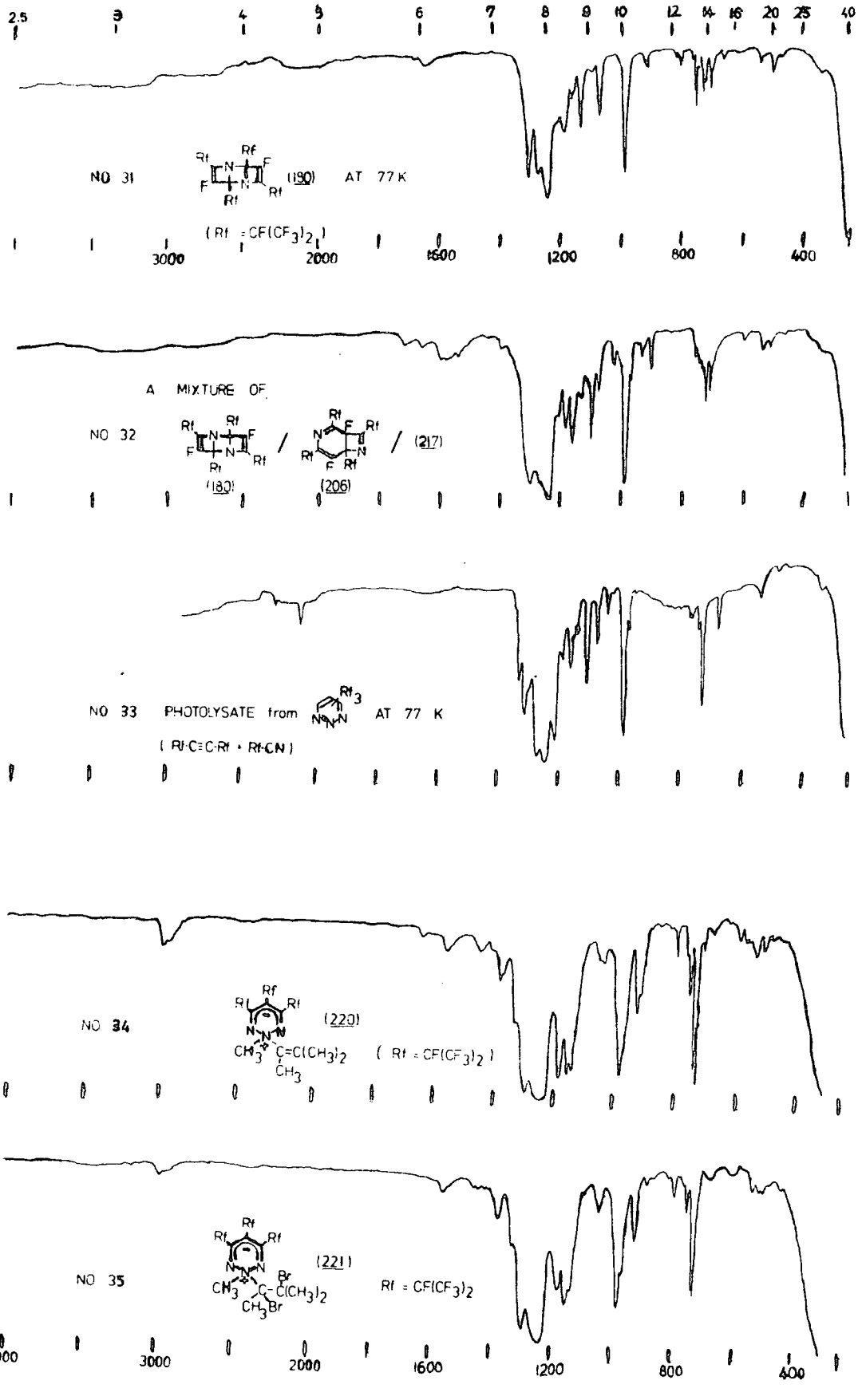

2·5 MICRONS 3.0
4.0
5.0
6.0
7.0
8.0
9.0
10
12
14
16
20
25
40
NO 5
Rf = CF(CF3)2
(166)
NO 7
Rf = CF(CF3)2
(167)
4000
3000
2000
1600
1200
800
400
NO 8
Rf = CF(CF3)2
(173)
NO 9
Rf = CF(CF3)2
(174)
NO. 10
Rf = CF(CF3)2
(169)
4000 CM-1
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400

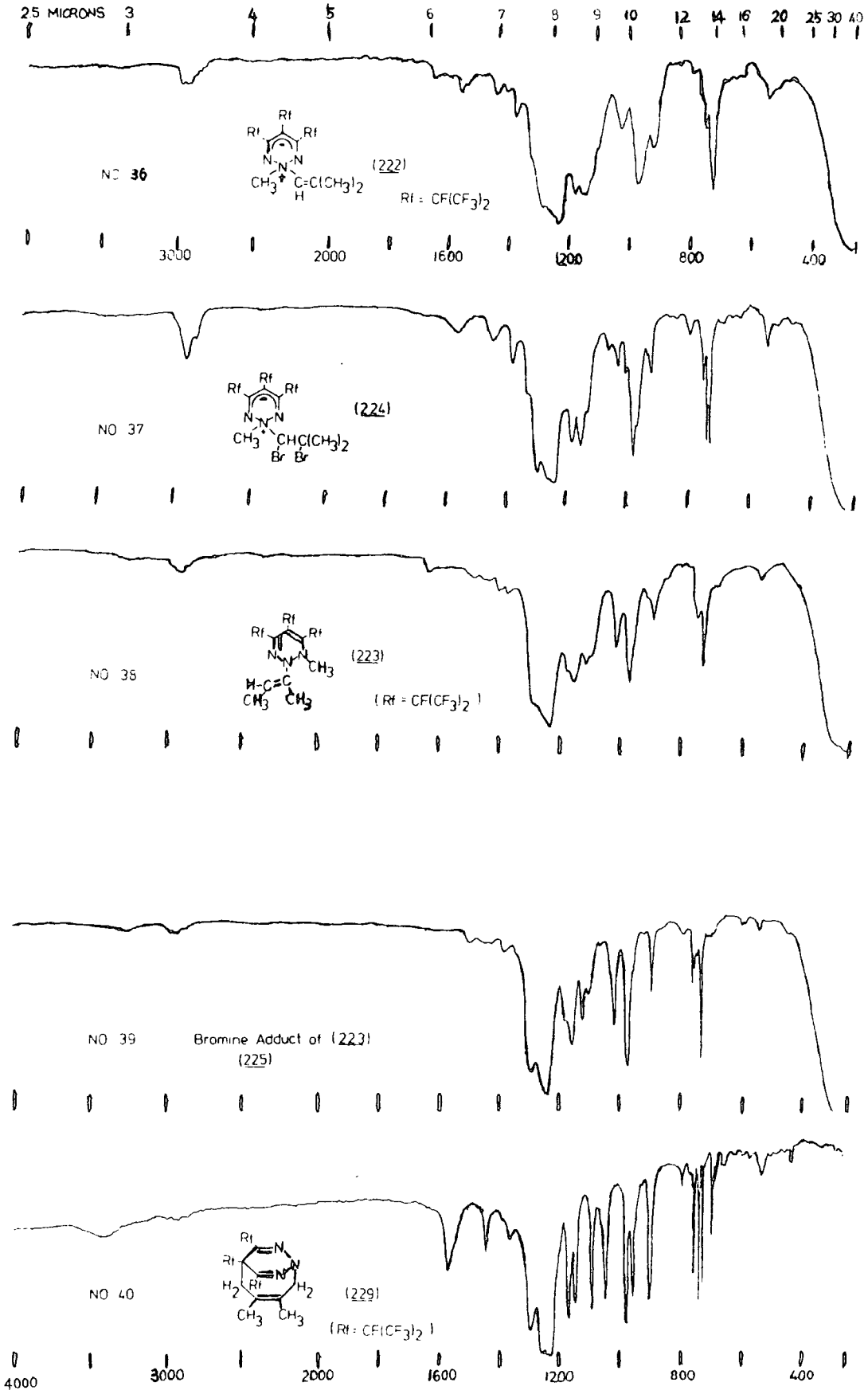

2.5 MICRONS 3.0 4.0 5.0 6.0 7.0 8.0 9.0 10 12 14 16 20 25 30 40
NO. 11
Rf = CF(CF3)2
(170)
NO. 12
CCl2=CCl-CN
(34)
4000 3000 2000 1600 1200 800 400
NO. 13
Rf = CF(CF3)2
(177)
NO. 14 (CF3)2CF-CN (46)
NO. 15 50/50 MIXTURE OF (CF3)2CF-C≡CF (179)
AND (CF3)2CF-CN (46)
4000 3000 2000 1600 1200 800 400


2.5
3
4
5
6
7
8
9
10
12
14
16
20
25
40
NO 16
(189)
4000
3000
2000
1600
1200
800
400
NO 17
(189)
NO 18
50/50 MIXTURE OF
(45)
AND
(46)
NO. 19
(193)
NO 20
52/48 MIXTURE OF
(194)
(195)


2.5
3
4
5
6
7
8
9
10
12
14
16
20
25
40
NO 21 POLY(C_3F_3N)
(201)
4000
3000
2000
1600
1200
800
400
NO. 22 POLY (C_3F_3N-co-C_4F_6)
(202)
NO 23
Rf
Rf
F
F
N
N
Rf
Rf
(180)
(Rf = $CF(CF_3)_2$)
NO 24
Rf
F
N
Rf
(209)
(Rf = $CF(CF_3)_2$)
60/40 MIXTURE OF
NO 25
Rf
F
H
H
N
O
Rf
H
(212)
/
Rf
N
O
Rf
F
(213)
4000
3000
2000
1600
1200
800
400


2·5
3
4
5
6
7
8
9
10
12
14
16
20
25
40
NO. 26
Rf = CF(CF3)2
(214)
3000
2000
1600
1200
800
400
NO. 27
(Rf = CF(CF3)2)
(204)
NO. 28
AND
AT 77K
(MINOR)
(175)
NO. 29.
AT 77K
(163)
NO. 30
PHOTOLYSATE from
AT 77K
(Rf = CF(CF3)2)
4000
3000
2000
1600
1200
800
400


2.5
3
4
5
6
7
8
9
10
12
14
16
20
25
40
NO 31
(190)
AT 77 K
(Rf = CF(CF3)2)
3000
2000
1600
1200
800
400
A MIXTURE OF
NO 32
/
/ (217)
(180)
(206)
NO 33
PHOTOLYSATE from
AT 77 K
(Rf-C≡C-Rf + Rf-CN)
NO 34
(220)
(Rf = CF(CF3)2)
NO 35
(221)
Rf = CF(CF3)2
4000
3000
2000
1600
1200
800
400


25 MICRONS 3 4 5 6 7 8 9 10 12 14 16 20 25 30 40
NO 36
(222)
Rf = CF(CF3)2
3000 2000 1600 1200 800 400
NO 37
(224)
NO 38
(223)
(Rf = CF(CF3)2)
NO 39
Bromine Adduct of (223)
(225)
NO 40
(229)
(Rf = CF(CF3)2)
4000 3000 2000 1600 1200 800 400

APPENDIX III

Mass Spectra

1. 4,5,6-Trichloro-1,2,3-triazine (157).
2. 4,5-Dichloro-6-fluoro-1,2,3-triazine (161).
3. 5-Chloro-4,6-difluoro-1,2,3-triazine (162).
4. 4,5,6-Trifluoro-1,2,3-triazine (163).
5. Perfluoro-4,6-bisisopropyl-1,2,3-triazine (164).
6. Perfluoro-4,5,6-trisisopropyl-1,2,3-triazine (165).
7. Perfluoro-2,4,6-trisisopropyl-5-isopropylidene-1,2,3-triazacyclohexa-3,6-diene (166).
8. 4,4-Bistrifluoromethyl-6,8,10-trisheptafluoroisopropyl-1,2,7,8,9-pentazaspiro[4,5]deca-2,6,9-triene (167).
9. 4,6-Bisheptafluoroisopropyl-2,5-bis(2′-trifluoromethyl-2′-methoxy-3′,3′,3′-trifluoropropyl)-1,2,3-triazacyclohexa-3,6-diene (173).
10. 2,4,6-Trisheptafluoroisopropyl-5-(1′,1′-bistrifluoromethyl-acetonyl)-1,2,3-triazacyclohexa-3,6-diene (174).
11. 2-Phenyl-4,6-bisheptafluoroisopropyl-5-heptafluoroisopropylidene-1,2,3-triazacyclohexa-3,6-diene (169).
12. Perfluoro-4,5,6-trisheptafluoroisopropyl-2-(cyclobut-1′-enyl)-1,2,3-triazacyclohexa-3,6-diene (170).
13. Trifluoroacrylonitrile (34).
14. Perfluoro-2,4,5-trisisopropylpyrimidine (177).
15. Perfluoro-3-methylbut-1-yne (179) and perfluoroisobutyronitrile (46). (50/50 mixture).
16. 1-Fluoro-2-heptafluoroisopropyl-4-methyl-4-(2′-methylprop-2′-enyl)-cyclobut-1-ene (188).
17. 1-Fluoro-2-heptafluoroisopropyl-4,5-dimethyl-cyclohexa-1,4-diene (189).

18. Perfluoro-2,5-dimethyl-4-isopropylhexa-2,3-diene (193).

19. Perfluoro-4,5-bisisopropyl-2,8-dimethylocta-2,3,5,6-tetraene (194) and perfluoro-6-isopropyl-2,5,5,8-tetramethylnona-6,7-diene-3-yne (195) (50/50 mixture).

20. Poly(trifluoroazete-co-hexafluorobut-2-yne) (202).

21. A 1:1 adduct of trifluoroazete with hexafluorobut-2-yne (203).

22. Perfluoro-2,4,6,8-tetrakisisopropyl-1,5-diazatricyclo-[4,2,0,$O^{2,5}$]octa-3,7-diene (180).

23. (Endo)-1-fluoro-3,4-bisheptafluoroisopropyl-4-aza-9-oxatricyclo[4,2,1,$O^{2,5}$]nona-3,7-diene (212) and (endo)-2-fluoro-7,9-bisheptafluoroisopropyl-8-aza-3-oxatricyclo-[5,2,0,$O^{2,6}$]nona-4,8-diene (213) (60/40 mixture).

24. 9-fluoro-1,8-bisheptafluoroisopropyl-7-aza-3-oxatricyclo-[5,2,0,$O^{2,5}$]nona-4,8-diene (214).

25. Trifluoroazete (175).

26. $\{(CF_3)_2CF\}_2\ C_3FN$.

27. $[\{(CF_3)_2CF\}_2\ C_3FN]_2$.

28. 2-(1',2'-dimethylprop-1'-enyl)-2-methyl-4,5,6-trisheptafluoroisopropyl-1,3-diaza-2-azaniacyclohexadienide (220).

29. 2-(2'-methylprop-1'-enyl)-2-methyl-4,5,6-trisheptafluoroisopropyl-1,3-diaza-2-azaniacyclohexadienide (222).

30. 2-(1'-methylprop-1'-enyl)-1-methyl-4,5,6-trisheptafluoroisopropyl-1,2,3-triazacyclohexa-3,5-diene (223).

31. 6,7,10-Trisheptafluoroisopropyl-3,4-dimethyl-1,8,9-triazabicyclo[4,2,2]deca-3,8,9-triene (229).

32. 2-(1',2'-Dibromo-1',2'-dimethylpropyl)-2-methyl-4,5,6-trisheptafluoroisopropyl-1,3-diaza-2-azaniacyclohexadienide (221).

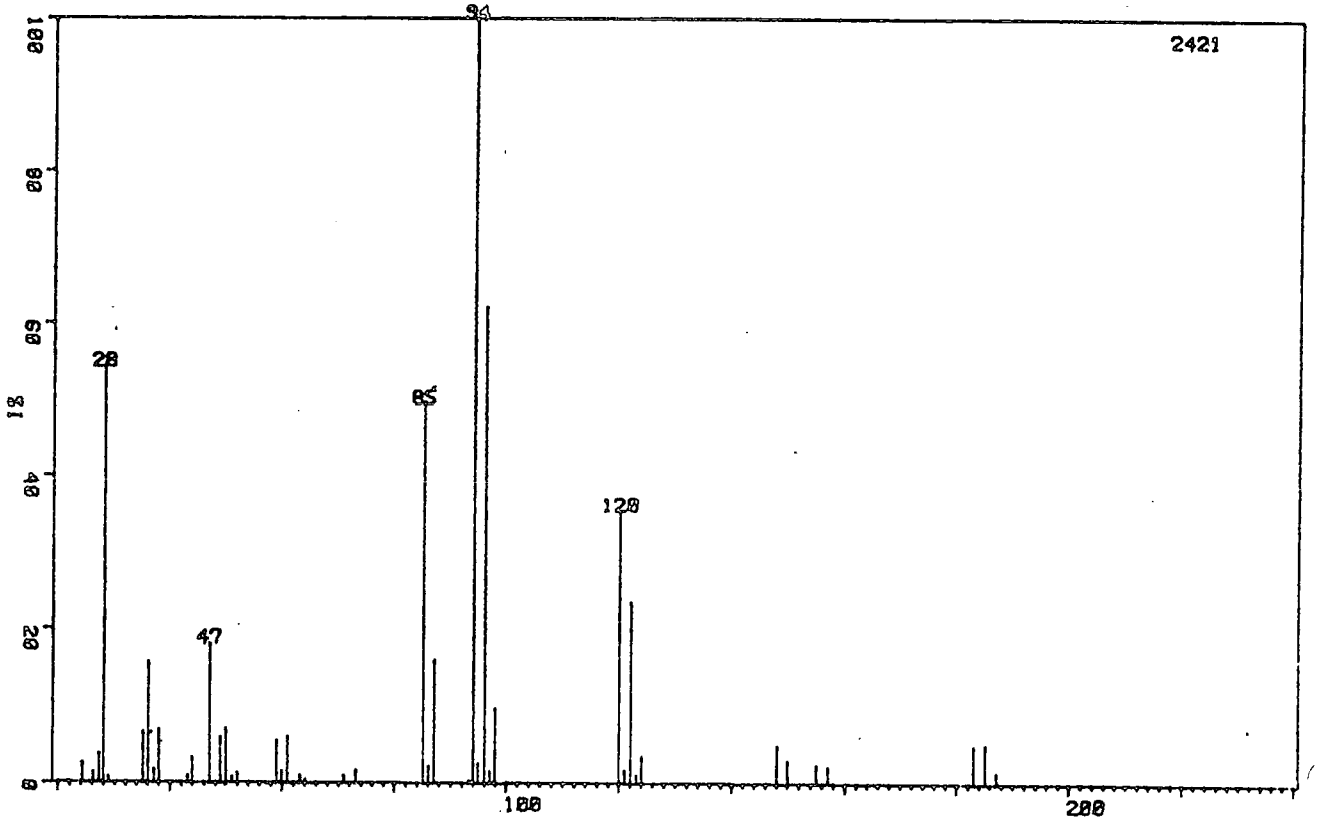
33. 2-(1',2'-Dibromo-2'-methylpropyl)-2-methyl-4,5,6-trisheptafluoroisopropyl-1,3-diaza-2-azaniacyclohexadienide (224).

34. 2-(1',2'-Dibromo-1'-methylpropyl)-1-methyl-4,5,6-trisheptafluoroisopropyl-1,2,3-triazacyclohexa-3,5-diene (225).

NO. 1

MTTCT 5 M.TAMURA
CAL:CAL8

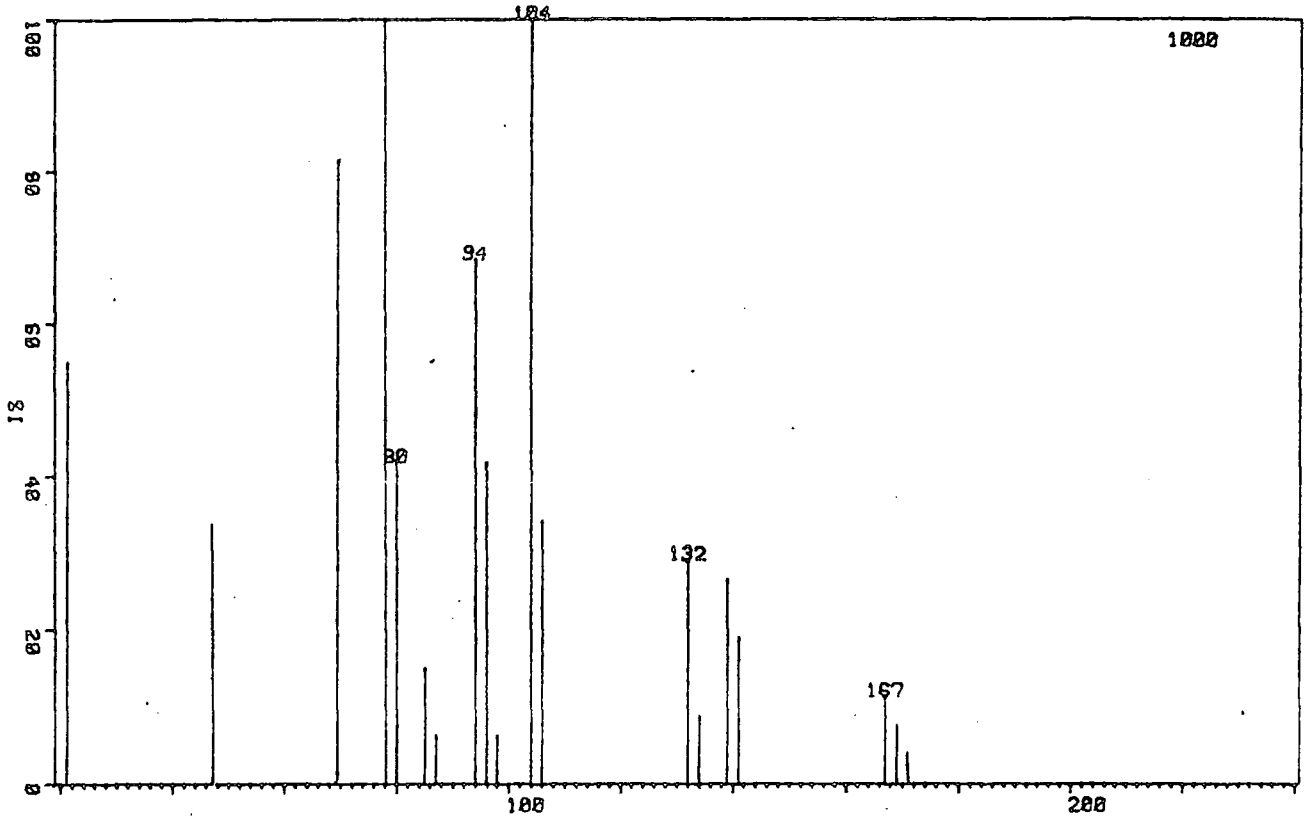
08-MAR-84



PEAK NO.	MASS	INT. PERF						
1	21.31	2.60	21	64.16	0.45			
2	26.30	1.32	22	71.00	0.92			
3	27.04	4.15	23	73.07	1.67			
4	28.12	53.23	24	85.05	9.48			
5	29.05	0.74	25	86.07	2.27			
6	39.10	6.03	26	87.04	15.97			
7	40.15	11.20	27	93.41	0.31			
8	42.10	1.75	28	94.03	100.00			
9	45.04	5.90	29	95.03	1.60			
10	46.11	0.95	30	96.04	2.12			
11	47.13	4.27	31	97.04	1.57			
12	47.07	19.15	32	98.00	7.79			
13	49.15	5.95	33	119.01	5.48			
14	52.39	2.19	34	121.03	3.78			
15	53.17	0.83	35	122.03	21.54			
16	55.06	1.29						
17	56.09	5.42						
18	59.03	1.53						
19	60.13	6.04						
20	61.09	0.95						

NO. 2

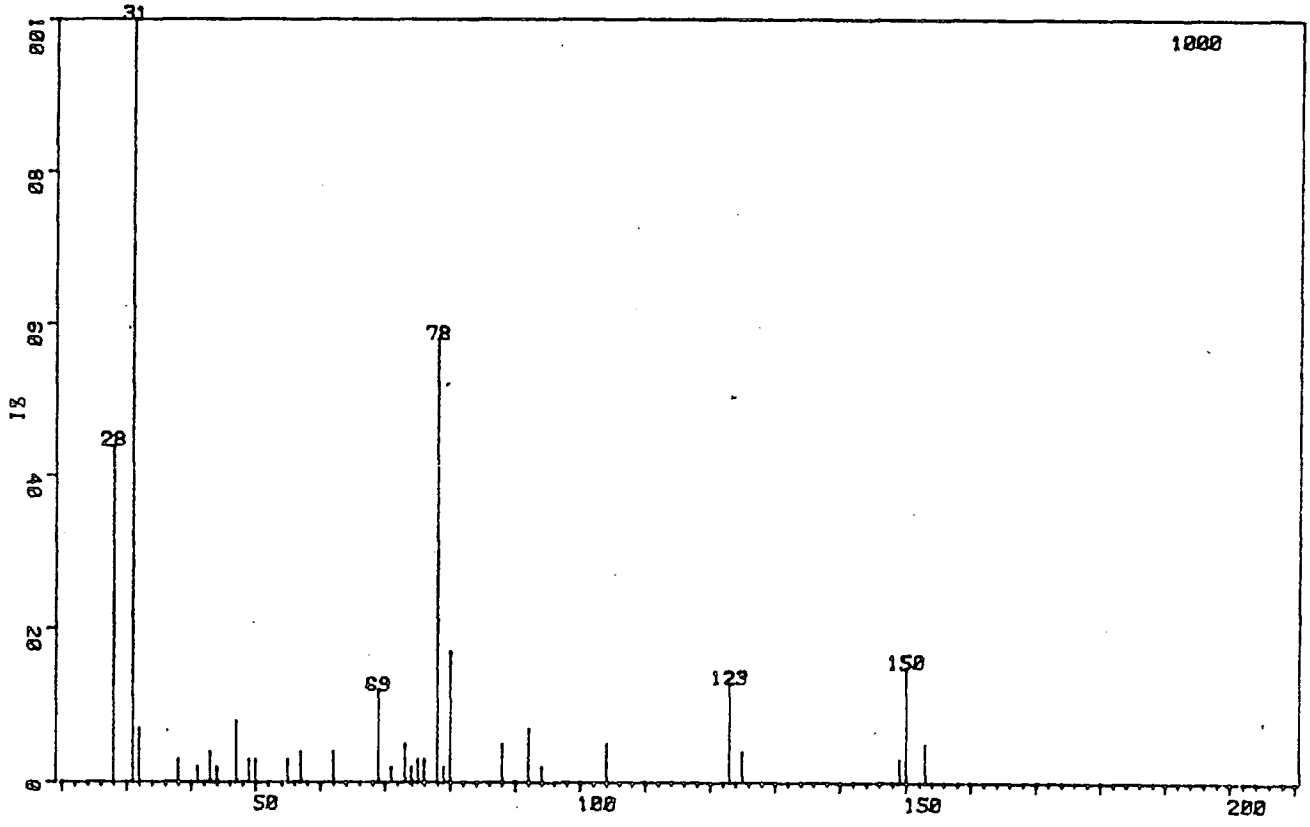
MT1014 Ø M.TAMURA MT10.14 23-FEB-84
CAL:LJB 0:0



peak No.	mass	%ht base
1	28.13	5.46
2	30.92	53.22
3	47.13	22.05
4	69.05	65.33
5	77.09	100.00
6	79.77	32.24
7	79.96	6.00
8	85.05	12.32
9	87.03	4.91
10	94.00	53.53
11	94.28	5.02
12	95.83	33.31
13	96.17	6.70
14	97.91	5.44
15	103.97	78.93
16	105.57	26.78
17	106.48	6.56
18	131.98	23.06
19	133.99	6.95
20	138.91	21.20
21	140.91	14.88
22	166.94	8.88
23	168.90	6.77
24	170.85	3.26

NO. 3

MTS384 Ø M.TAMURA MTS3.84 23-FEB-84
CAL:LIB 0:0



PEAK NO.	MASS	%HT. BASE
1	28.14	43.97
2	30.91	100.00
3	32.02	7.41
4	38.08	3.45
5	40.98	1.90
6	43.11	3.62
7	44.13	1.90
8	47.06	8.45
9	48.93	3.10
10	49.88	2.59
11	55.15	2.59
12	57.12	3.79
13	62.01	4.14
14	68.96	11.90
15	71.03	1.90
16	73.00	4.66
17	74.04	2.24
18	75.02	2.59
19	76.08	2.59
20	77.94	57.93
21	78.93	2.41
22	79.84	17.24
23	87.99	5.17
24	91.96	7.07
25	94.00	2.07
26	104.01	5.00
27	122.94	12.59
28	124.95	4.31
29	148.88	3.10
30	150.84	15.00
31	152.95	5.17

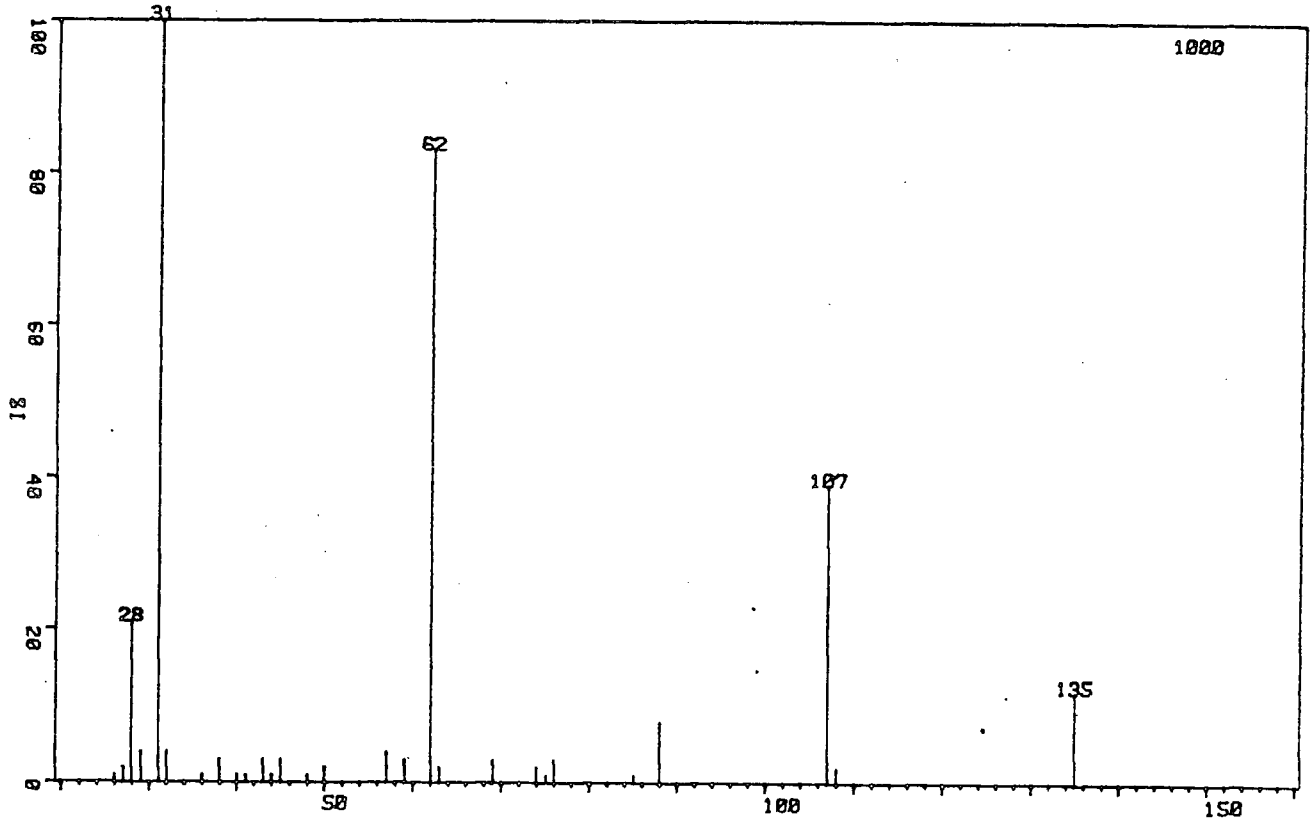
NO. 4

MT6580 0 M.TAMURA MT6S.80

CAL:L1B

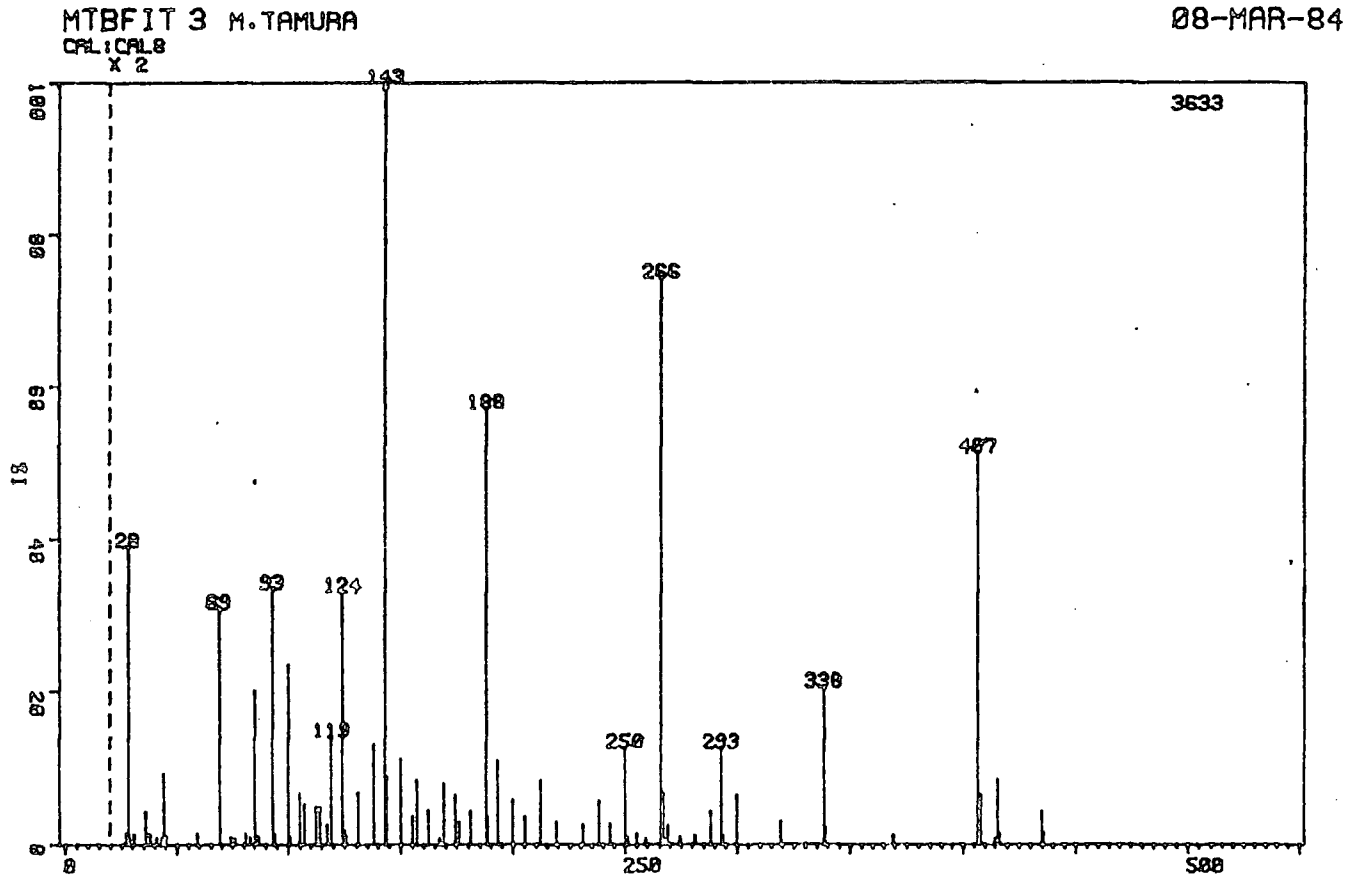
23-FEB-84

0:0

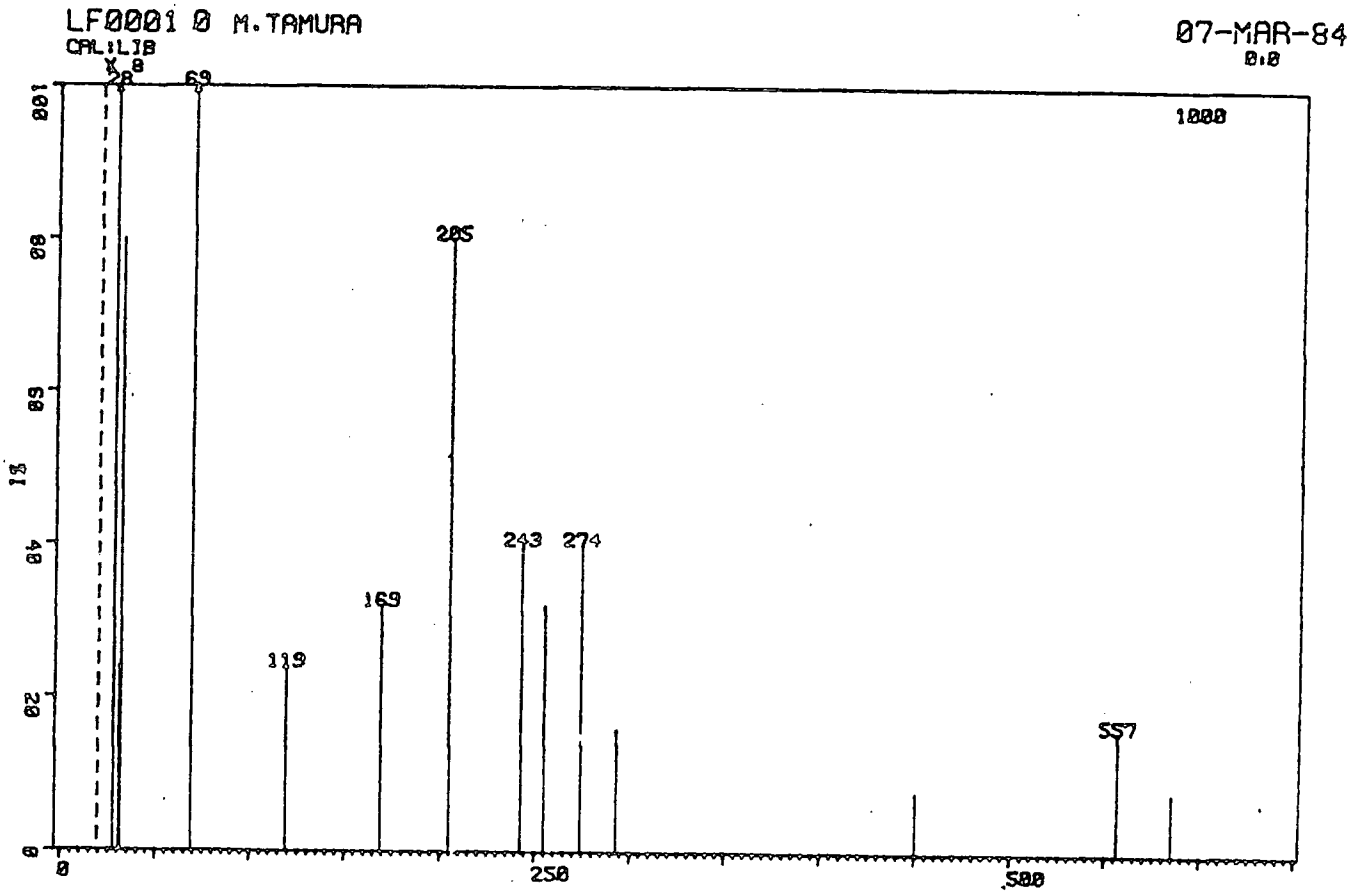


PEAK NO.	MASS	%HT. BASE
1	24.30	0.55
2	27.26	2.24
3	28.14	20.54
4	29.03	4.44
5	30.91	100.00
6	32.05	3.56
7	36.17	0.55
8	38.07	2.60
9	39.86	0.59
10	41.00	0.88
11	43.10	2.97
12	44.16	0.77
13	45.16	2.53
14	48.05	0.55
15	49.88	1.50
16	57.10	3.89
17	59.04	2.86
18	61.67	0.40
19	62.04	83.13
20	62.17	6.42
21	63.03	1.72
22	68.97	3.34
23	74.12	1.80
24	75.09	1.03
25	76.04	3.09
26	85.03	1.21
27	85.19	0.49
28	87.97	7.66
29	106.95	59.05
30	107.16	2.97
31	107.90	1.69
32	134.97	11.99

NO. 5

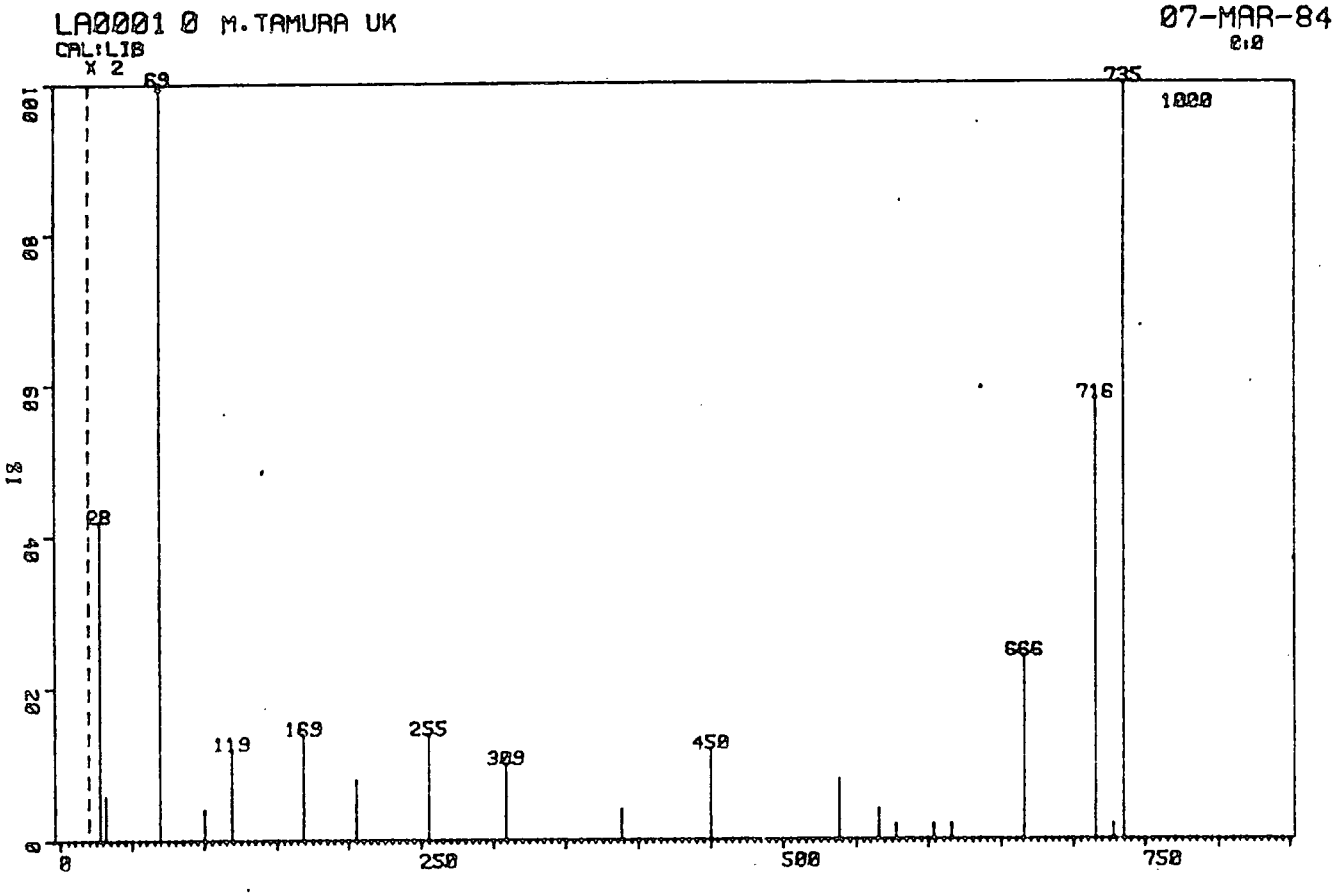

MTBFIT 3 M.TAMURA
08-MAR-84
CAL:CAL8
X 2
143
3633
266
188
407
28
89
93
124
119
338
250
293
%
0
250
500

NO. 6



PEAK NO.	MASS	%HT. BASE
1	28.13	39.54
2	30.91	2.53
3	32.02	9.89
4	69.01	100.00
5	119.05	2.66
6	169.14	4.18
7	205.15	9.89
8	243.18	4.94
9	255.11	3.93
10	274.14	4.44
11	293.20	2.28
12	450.35	1.39
13	557.23	2.03
14	584.87	0.40

NO. 7

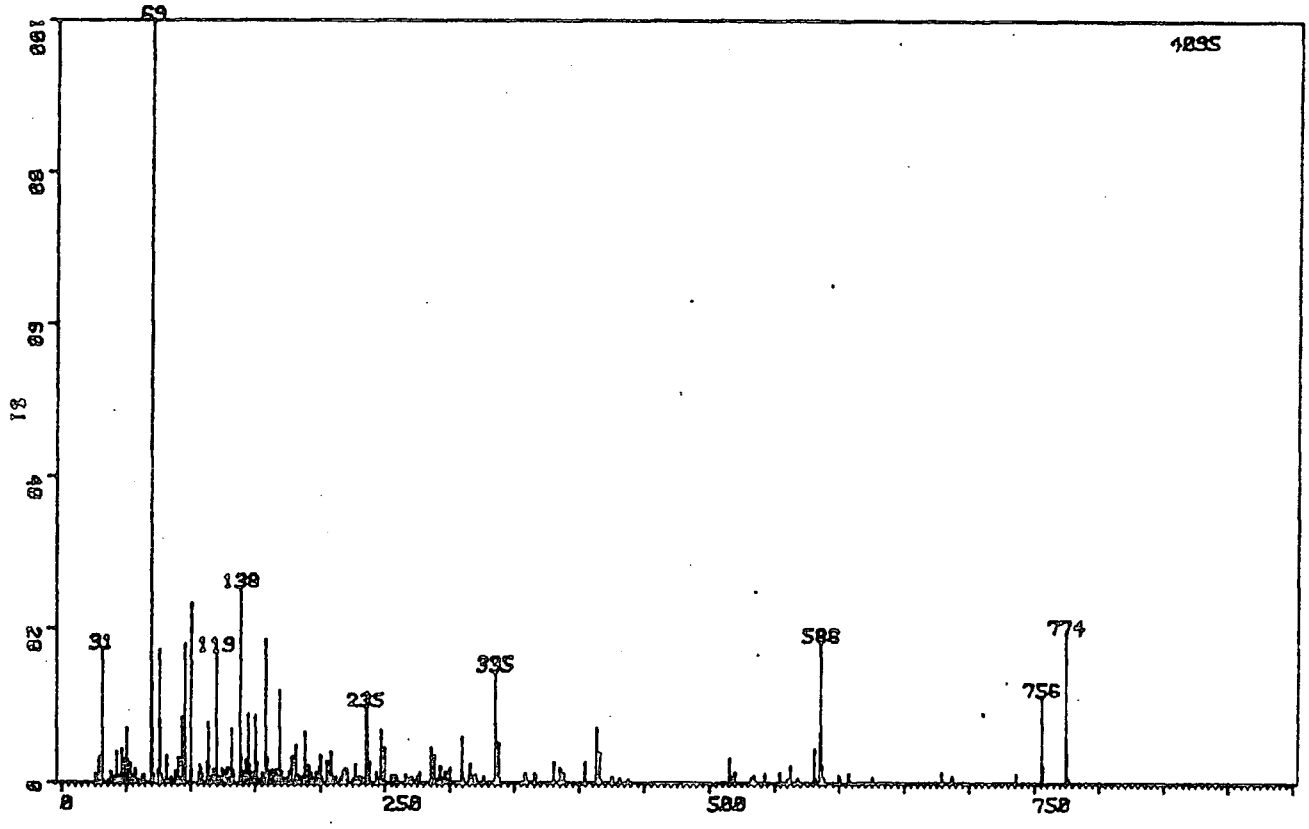


PEAK NO.	MASS	%HT. BASE
1	28.13	20.96
2	30.89	0.37
3	32.01	3.16
4	40.97	0.34
5	43.12	0.88
6	44.12	0.78
7	45.17	0.44
8	68.97	100.00
9	69.91	1.05
10	85.01	0.85
11	99.93	2.24
12	114.05	0.75
13	118.97	6.28
14	131.00	0.41
15	149.95	3.12
16	157.01	1.15
17	164.01	0.75
18	168.97	7.30
19	176.04	0.82
20	180.97	2.28
21	205.03	3.97
22	212.03	0.37
23	218.98	0.37
24	223.99	0.44
25	235.97	0.37
26	243.02	0.88
27	250.00	0.68
28	255.02	6.79
29	256.05	0.51
30	274.05	0.85
31	281.00	0.48
32	293.03	1.56
33	300.00	2.14
34	305.08	0.68
35	308.97	4.82
43	387.88	2.17
44	399.90	1.70
45	440.05	0.31
46	450.05	5.50
47	468.99	0.61
48	488.02	0.99
49	491.01	0.54
50	527.95	0.78
51	538.12	4.11
52	553.99	0.65
53	566.08	1.90
54	578.18	0.92
55	600.07	0.51
56	604.03	0.58
57	615.83	0.58
58	628.00	0.37
59	647.61	0.31
60	665.95	12.33
61	715.93	28.77
62	728.46	0.34
63	735.02	49.59

NO. 8

MT91 S M.TAMURA
CAL:CC

26-JUN-83

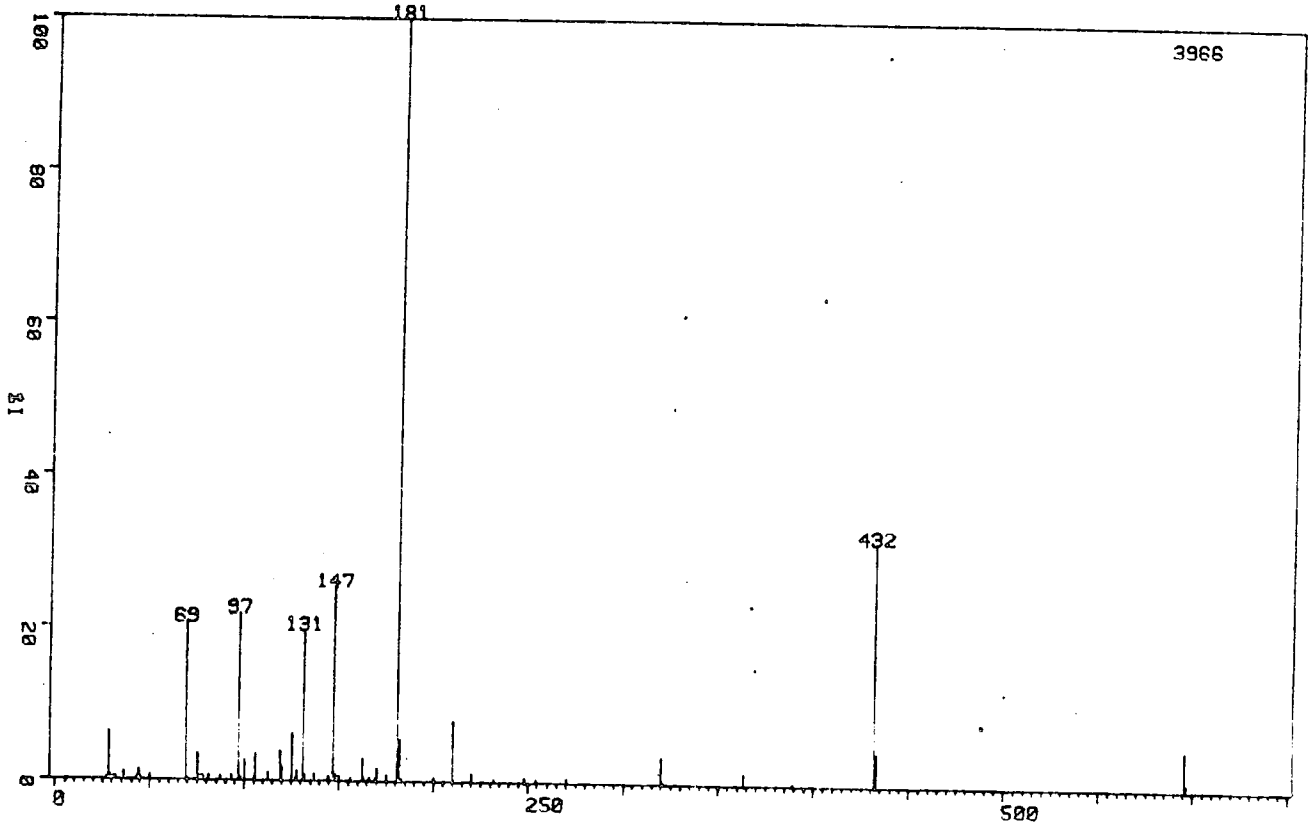


PEAK NO.	MASS	%HT. BASE
3	28.06	3.05
4	28.93	3.32
5	30.81	17.46
31	68.94	100.00
32	69.91	13.14
33	70.98	1.10
34	74.05	1.68
35	75.05	17.22
36	76.05	8.08
48	92.99	8.50
49	94.03	1.44
50	95.02	17.95
51	96.03	2.95
52	98.95	2.17
53	99.89	23.22
65	118.97	17.09
66	119.96	5.40
75	130.97	6.94
79	138.01	25.45
80	138.98	3.35
81	139.98	1.54
85	144.03	8.96
86	145.05	2.30
87	146.04	1.42
96	157.98	18.49
97	158.99	3.25
106	168.98	12.09
107	169.97	1.44
153	235.01	9.96
154	236.02	11.87
155	237.03	2.22
156	238.00	2.71
194	334.95	14.68
195	335.97	1.44
196	337.85	5.20
206	412.88	7.20
207	414.02	0.90
208	415.90	3.83
213	515.69	3.20
214	516.93	0.71
215	519.82	1.29
223	562.72	2.25
225	580.66	4.42
226	581.99	0.56
227	584.73	6.45
228	585.86	18.34
229	586.96	2.32
230	588.02	0.66
231	599.87	1.00
232	600.89	0.56
233	607.76	1.22
234	625.76	0.68
235	679.20	1.39
236	687.17	0.90
237	736.20	1.20
238	755.63	11.48
239	756.85	2.30
240	774.29	19.51
241	775.37	3.69
242	776.38	0.56

NO. 9

MT145 4 M.TAMURA
CAL:CAL10

10-JAN-84

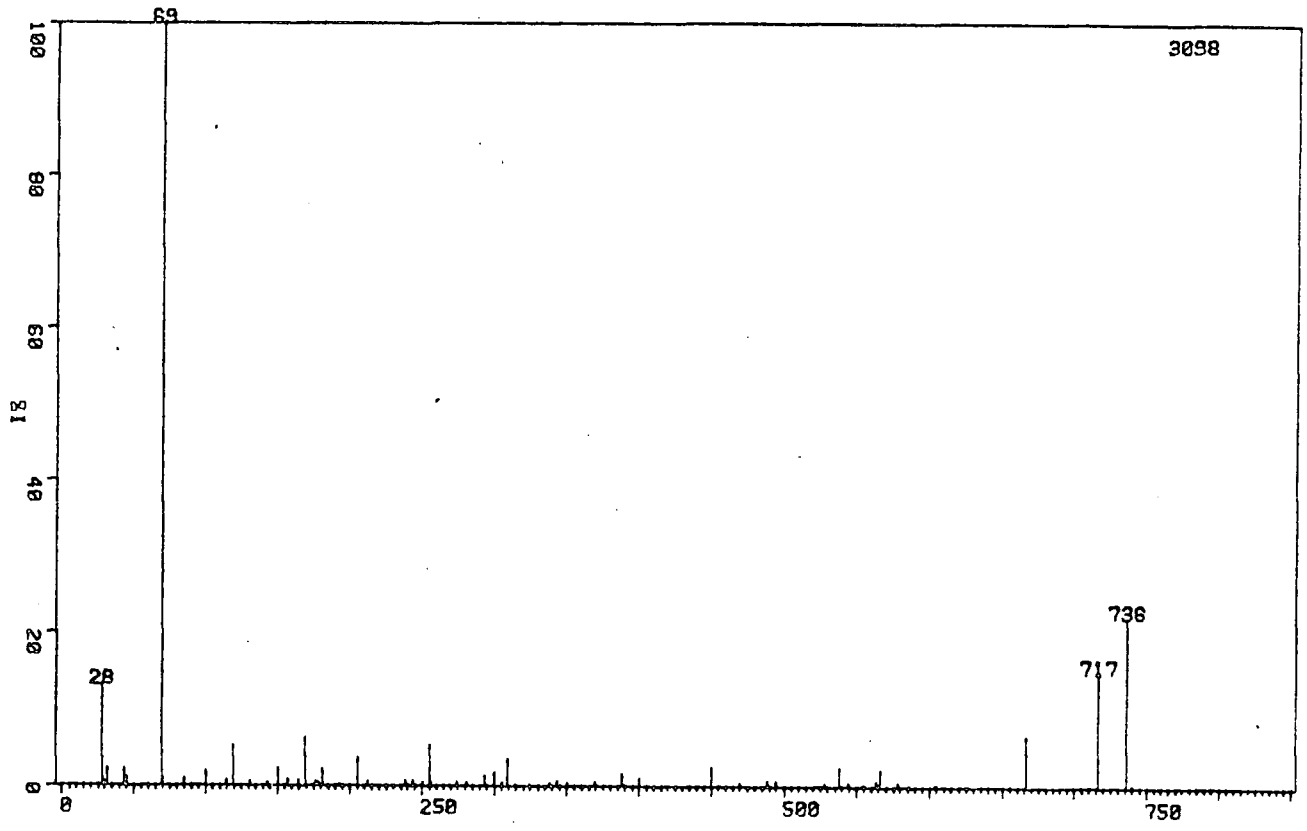


PEAK NO.	MASS	%HT. BASE
1	27.26	0.38
2	28.13	6.30
11	69.05	20.60
12	70.01	0.35
13	75.16	3.43
20	97.05	31.81
21	98.02	0.48
22	99.96	2.60
23	105.16	0.38
24	106.09	3.38
25	113.11	1.06
26	119.01	3.83
27	129.00	1.79
28	131.10	6.15
29	133.11	0.49
30	145.07	1.34
31	147.05	12.59
32	153.11	0.71
33	167.07	4.29
34	169.10	0.63
35	181.05	25.32
39	182.08	3.05
45	181.01	100.00
46	181.96	5.45
47	183.07	0.40
48	200.08	0.56
49	210.04	7.99
50	220.11	1.13
55	319.99	3.45
56	321.07	0.35
57	363.06	1.56
58	389.00	3.43
59	431.05	41.05
60	432.08	1.76
61	595.21	5.69
62	596.29	1.11

NO. 10

MT124 88 M.TAMURA
CAL:CALM12

18-OCT-83

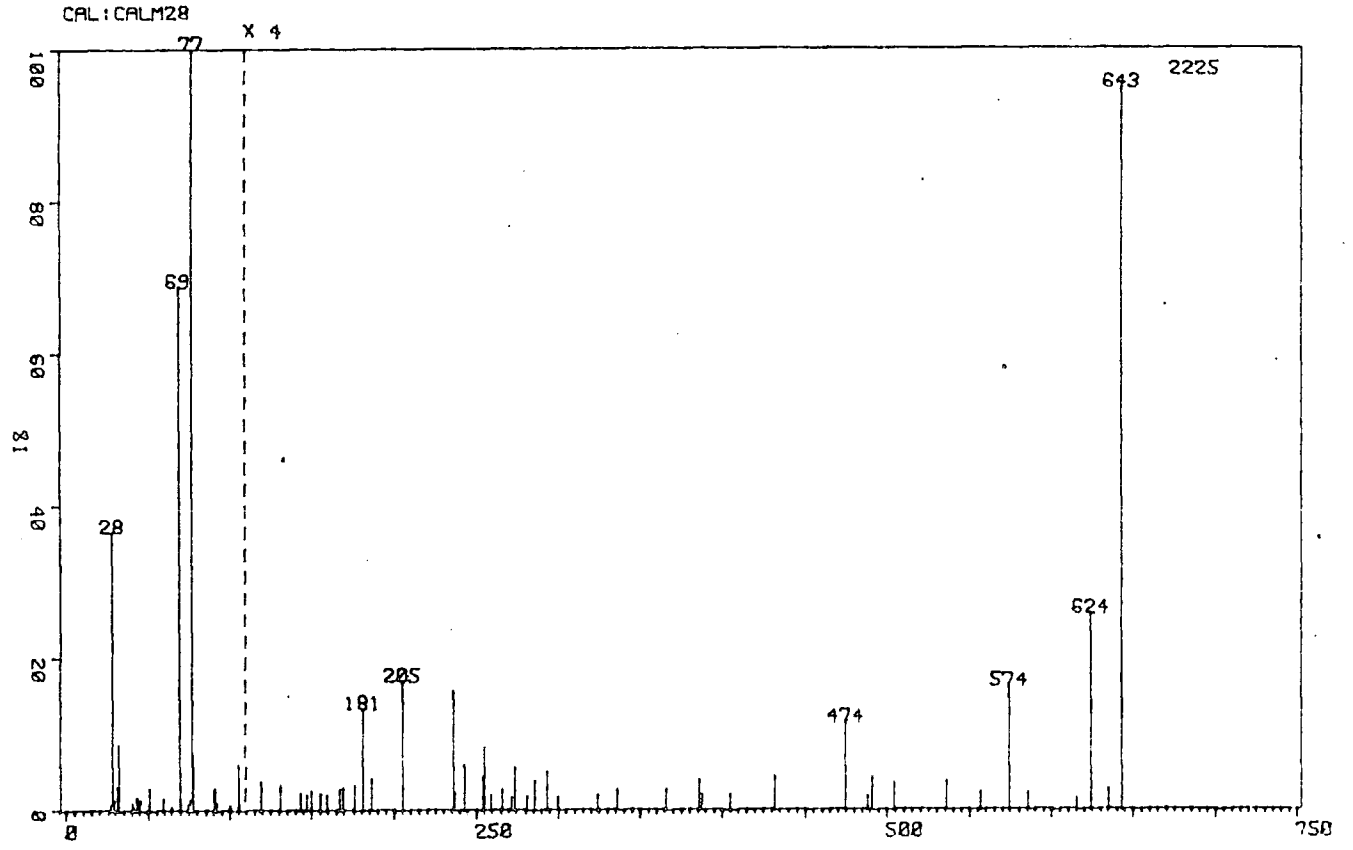


PEAK NO.	MASS	%HT. BASE						
1	28.06	13.20	21	178.07	0.48	41	349.92	0.42
2	28.93	0.77	22	181.03	2.16	42	369.07	0.58
3	30.84	0.48	23	193.06	0.36	43	388.07	1.61
4	31.95	2.29	24	205.09	3.74	44	400.07	1.13
5	43.10	2.26	25	212.08	0.65	45	450.11	2.52
6	44.13	0.87	26	238.11	0.65	46	469.18	0.45
7	45.17	1.10	27	243.09	0.65	47	488.20	0.74
8	68.99	100.00	28	250.12	0.48	48	494.17	0.74
9	69.94	1.13	29	255.10	5.33	49	528.25	0.48
10	85.09	0.94	30	256.11	0.55	50	538.25	2.49
11	99.98	1.90	31	274.07	0.55	51	544.11	0.52
12	114.12	0.74	32	281.10	0.55	52	554.19	0.42
13	119.00	5.23	33	293.07	1.32	53	563.04	0.77
14	131.06	0.52	34	300.04	1.84	54	566.20	2.23
15	143.07	0.48	35	305.11	0.55	55	578.15	0.55
16	149.99	2.32	36	309.03	3.52	56	586.05	0.36
17	157.07	0.90	37	314.12	0.36	57	604.35	0.39
18	164.08	0.74	38	324.07	0.36	58	666.48	6.68
19	169.03	6.26	39	338.12	0.48	59	716.54	14.88
20	176.12	0.61	40	343.08	0.74	60	736.17	22.08
						61	739.59	0.32

NO. 11

MT1467 M.TAMURA
CAL:CALM28

28-NOV-83

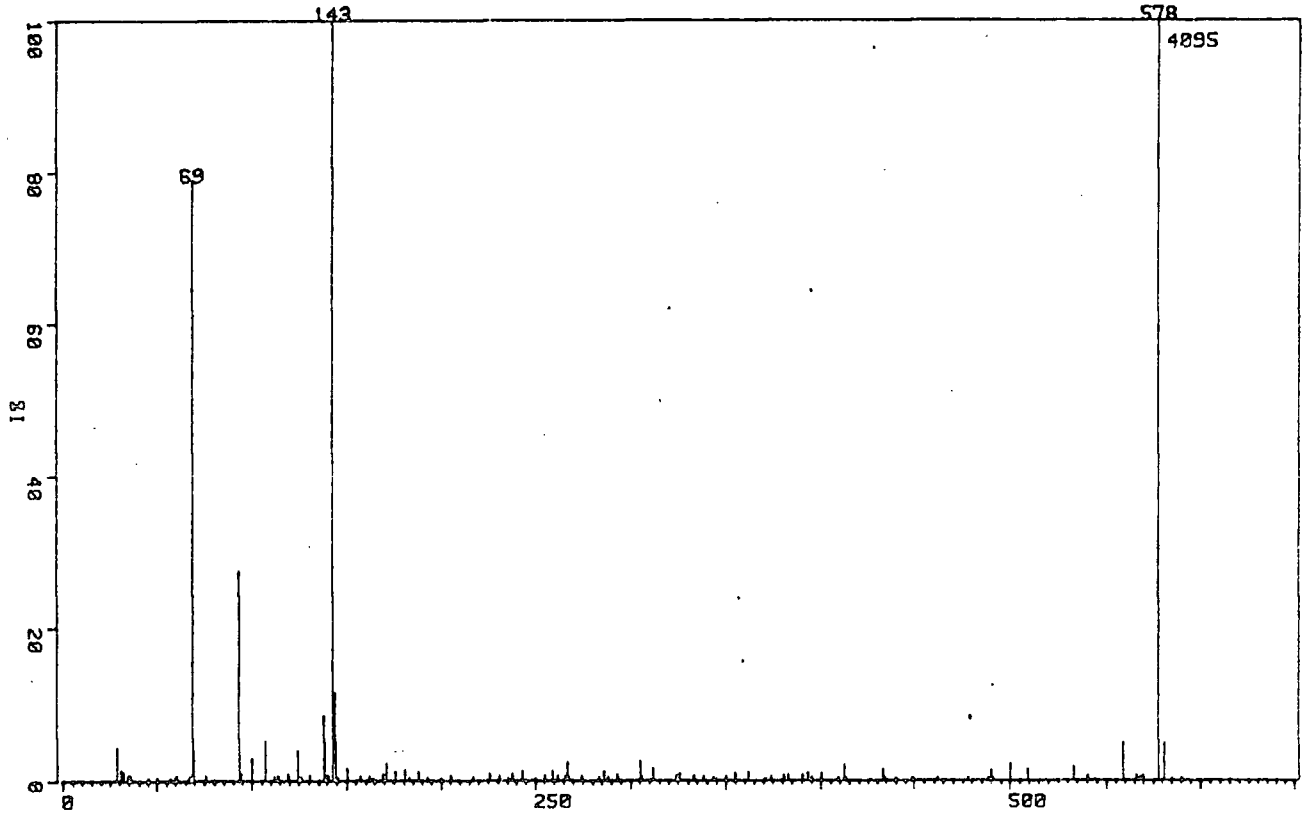


PEAK NO.	MASS	%HT. BASE
1	27.19	0.76
2	28.06	36.54
3	28.95	1.44
4	30.85	3.19
5	31.94	8.58
15	68.98	68.72
16	69.92	0.99
17	74.15	0.85
18	75.08	0.49
19	76.07	1.39
20	77.07	100.00
21	78.03	7.37
22	89.93	2.61
23	90.98	2.92
24	92.03	0.94
25	99.90	0.63
26	105.10	6.02
38	180.99	[illegible]
39	186.04	1.03
40	205.01	4.22
41	236.05	3.91
42	237.04	0.58
43	242.98	1.48
44	254.00	1.08
45	254.98	2.07
46	258.97	0.49
47	266.03	0.67
48	272.05	0.40
49	273.99	1.39
50	281.06	0.45
51	286.04	0.94
52	293.03	1.26
53	300.07	0.45
54	324.06	0.49
55	336.14	0.67
56	365.99	0.67
57	386.10	0.99
58	387.86	0.49
59	405.17	0.49
60	432.10	1.12
61	474.40	2.88
62	488.03	0.45
63	491.00	1.08
64	503.98	0.90
65	535.93	0.94
66	556.96	0.58
67	574.09	4.04
68	585.99	0.58
69	615.60	0.36
70	624.06	6.43
71	634.95	0.67
72	643.08	23.69

NO. 12

MT94 41 M.TAMURA
CAL:CALM18

19-MAY-83

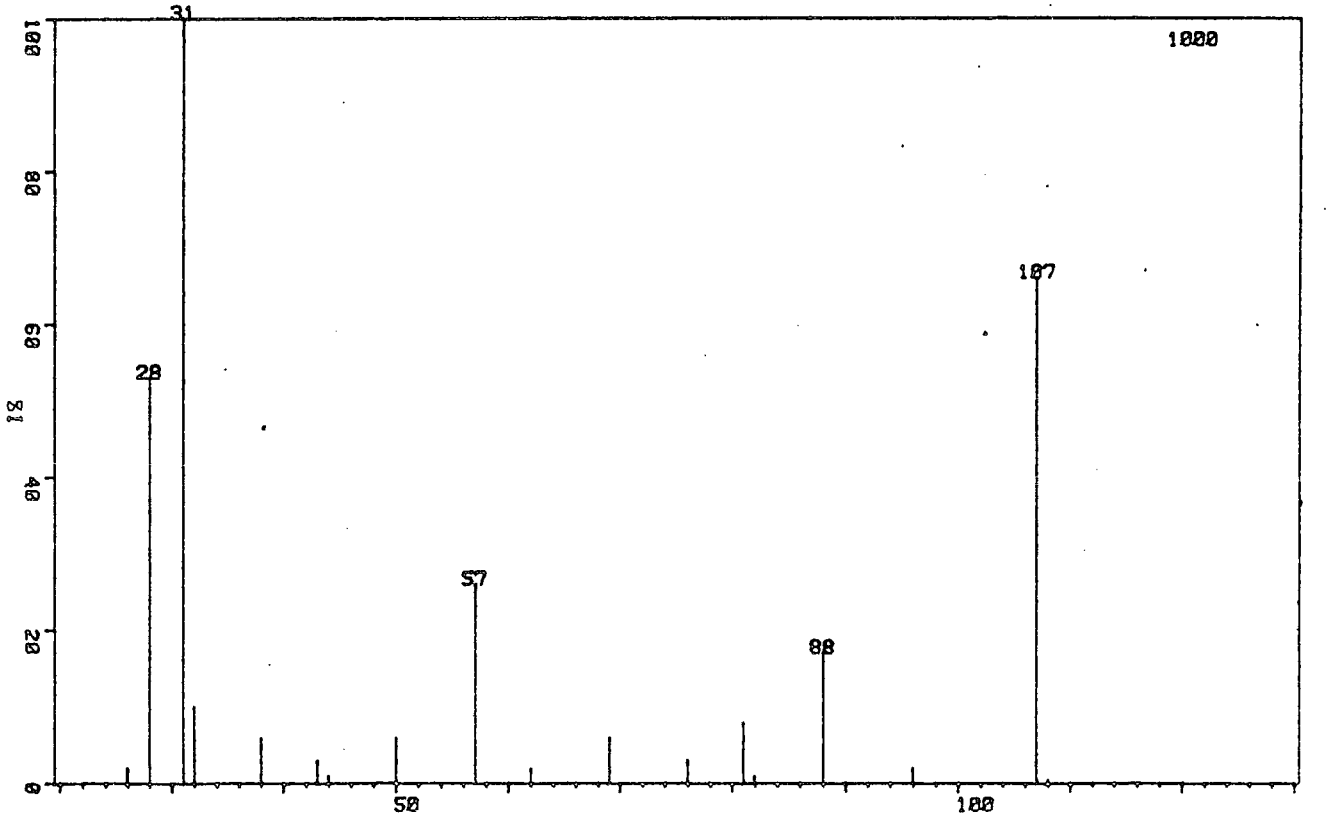


PEAK NO.	MASS	%HT. BASE						
1	28.13	14.46	67	142.85	100.00	141	428.07	0.32
2	30.91	3.66	68	143.81	16.61	142	431.10	0.51
3	32.02	3.17	69	144.61	4.64	143	433.10	1.68
34	69.03	100.00	70	145.53	0.56	150	490.20	2.64
35	69.20	3.15	78	169.00	1.44	151	499.99	2.49
45	93.02	61.34	79	170.98	4.20	152	502.18	0.37
46	93.44	0.34	80	176.04	3.83	153	509.09	2.32
47	93.69	0.46	81	180.98	4.18	154	533.00	2.27
48	94.01	2.42	114	304.89	3.79	155	534.17	0.24
49	99.94	5.59	115	306.09	0.66	156	540.06	0.71
50	101.01	0.39	116	311.97	2.81	157	557.21	0.34
51	107.03	12.38	117	313.02	0.54	158	558.93	5.64
54	114.06	1.51	118	323.97	0.95	159	566.02	0.27
55	118.99	3.08	119	325.90	1.34	160	577.81	100.00
56	119.98	0.56	120	332.96	1.03	161	581.07	5.84
57	124.03	8.67	121	337.90	1.05	162	586.20	0.37
58	125.07	0.81	125	350.03	1.05	163	589.92	0.32
59	126.07	0.81	126	355.06	1.10	164	597.48	0.32
60	130.94	2.81	127	361.97	1.12			
61	137.97	15.26	137	409.03	0.68			
62	138.22	2.95	138	412.09	2.15			

NO. 13

MT6SS Ø M.TAMURA MT6S.S
CAL:LIB

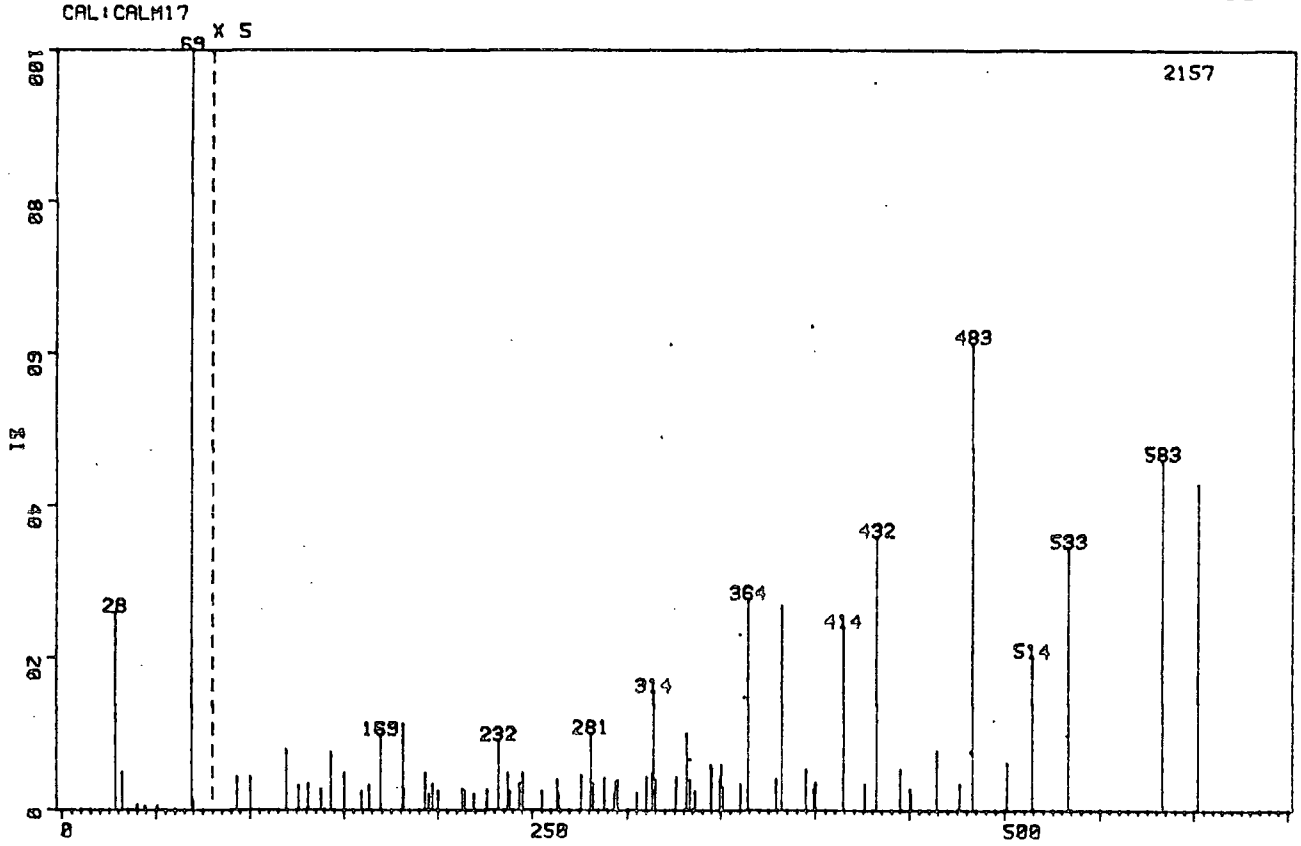
23-FEB-84
Ø:Ø



PEAK NO.	MASS	%HT. BASE
1	26.30	1.67
2	28.14	53.15
3	30.92	100.00
4	32.03	9.52
5	38.08	5.92
6	43.16	2.70
7	44.16	1.29
8	49.90	6.31
9	57.12	25.87
10	62.07	1.93
11	69.05	6.65
12	76.19	4.35
13	81.05	7.85
14	82.10	1.42
15	88.03	16.60
16	96.14	1.67
17	107.00	65.77

NO. 14

MT108 64 M.TAMURA 108 MASS MAX 23-JUN-83
CAL:CALM17

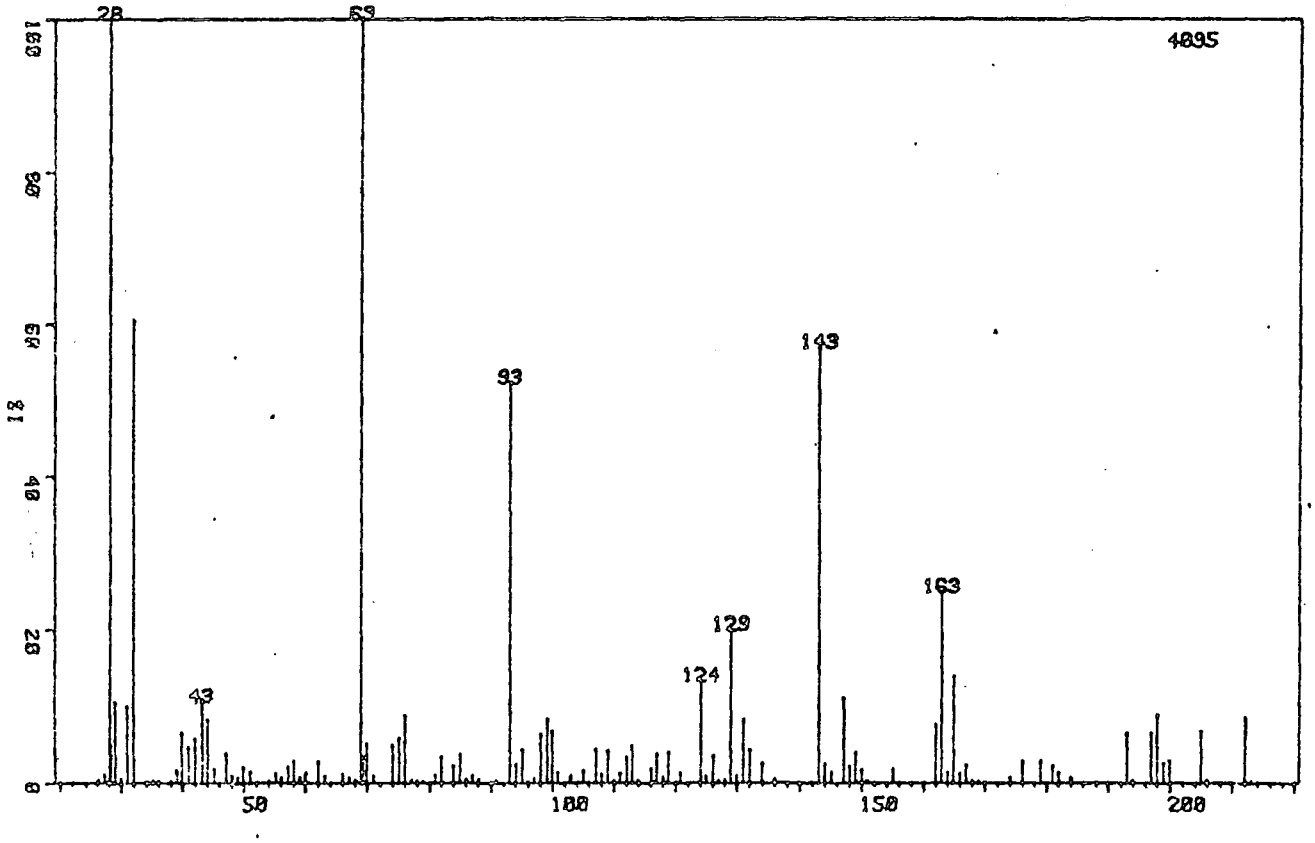


PEAK NO.	MASS	%HT. BASE
1	28.13	26.10
2	32.01	5.05
3	39.83	0.65
4	44.13	0.51
5	50.97	0.56*
6	68.99	100.00*
7	69.93	1.34*
10	119.03	1.62
11	126.14	0.65*
12	131.03	0.70*
13	138.05	0.56*
14	143.09	1.53*
18	169.02	1.99*
19	181.03	2.27
20	182.09	0.56
21	193.10	0.97
29	232.04	1.85*
30	237.06	0.97*
38	281.04	2.04*
39	282.14	0.70*
47	314.05	3.11
48	315.05	0.79*
49	326.08	0.88
50	331.56	2.04*
51	333.08	0.79*
52	336.11	0.51*
53	344.10	1.21
54	345.11	1.11*
55	348.99	0.79
56	349.98	1.21*
57	350.99	0.60*
58	359.98	0.70*
59	364.13	5.56
60	378.97	0.83*
61	382.08	5.38
62	394.52	1.07
65	414.24	4.82
66	425.94	0.70
67	432.07	7.19*
68	444.44	1.07
71	463.98	1.58
72	476.06	0.70
73	482.91	12.29
74	501.00	1.25
75	514.09	4.03
76	533.15	6.91
77	583.07	9.23
78	602.20	8.58

NO. 15

MTAC 5 M.TAMURA
CAL:CALM13

13-MAR-84

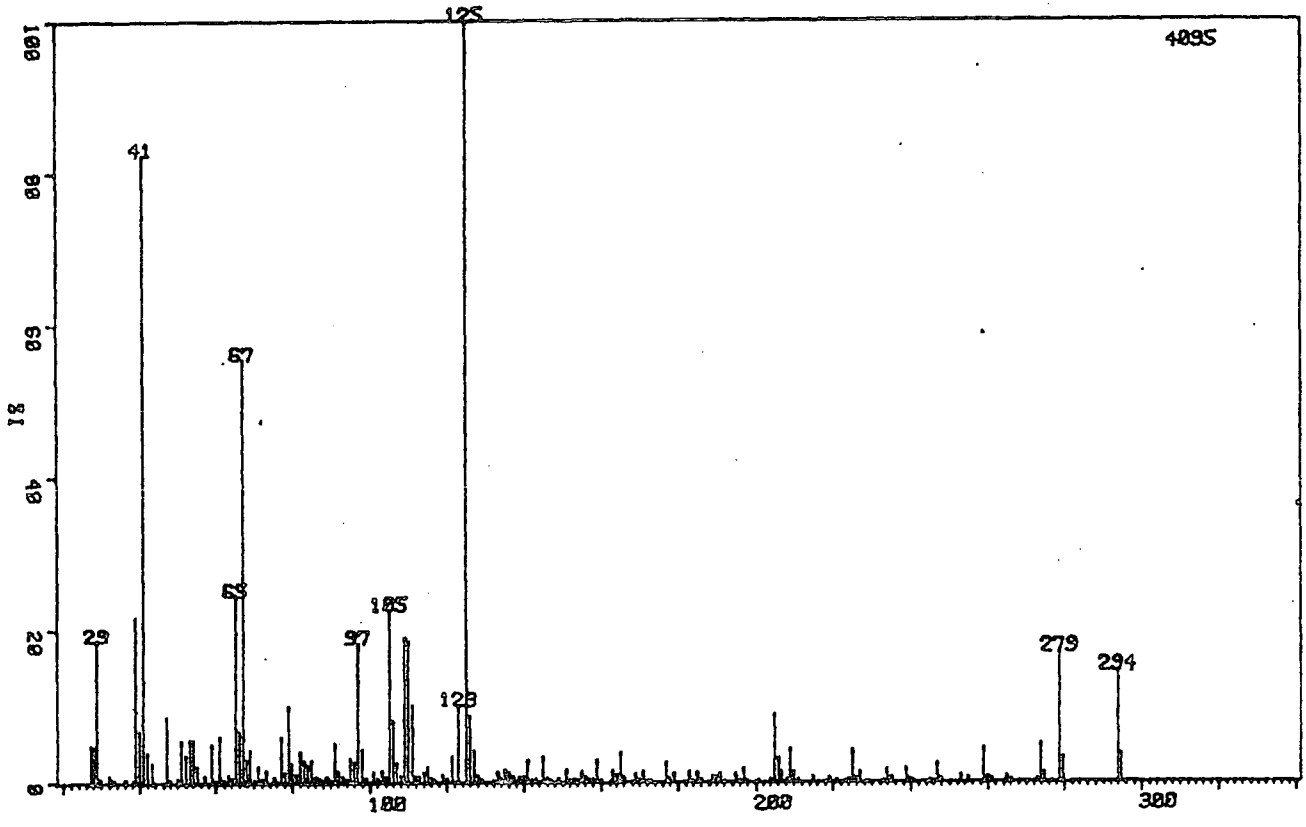


PEAK NO.	MASS	INT. RASE
4	28.07	100.00
5	28.16	4.88
6	28.44	0.37
7	28.94	1.50
8	29.39	0.71
9	30.84	2.96
10	31.95	60.63
16	39.81	6.47
17	40.96	4.69
18	42.05	5.69
19	43.09	10.57
20	44.13	8.33
40	68.96	100.00
41	69.17	3.39
42	69.87	5.56
43	70.99	0.70
44	74.04	4.86
45	75.06	5.79
46	76.03	8.77
58	93.00	52.23
59	94.01	2.52
60	95.05	4.40
61	96.06	0.52
62	96.50	0.61
63	98.02	4.30
64	99.03	0.25
65	99.92	6.24
80	118.90	3.98
81	120.87	1.39
82	124.05	13.41
87	128.96	19.88
88	129.94	0.35
89	130.95	3.28
90	131.96	4.32
91	133.98	2.64
92	135.99	0.54
93	143.03	56.92
94	144.04	2.44
95	145.05	1.39
96	147.01	11.11
102	162.00	0.[illegible]
103	163.02	1.[illegible]
104	164.03	0.[illegible]
105	165.04	0.[illegible]
106	175.01	0.[illegible]
107	178.03	0.[illegible]
118	196.02	0.[illegible]
119	197.00	0.[illegible]
120	198.02	0.[illegible]
121	199.02	0.[illegible]
122	200.03	0.[illegible]
123	201.04	0.[illegible]
124	202.04	0.[illegible]

NO. 16

MT1S928 M.TAMURA
CAL:CALM28

08-DEC-83

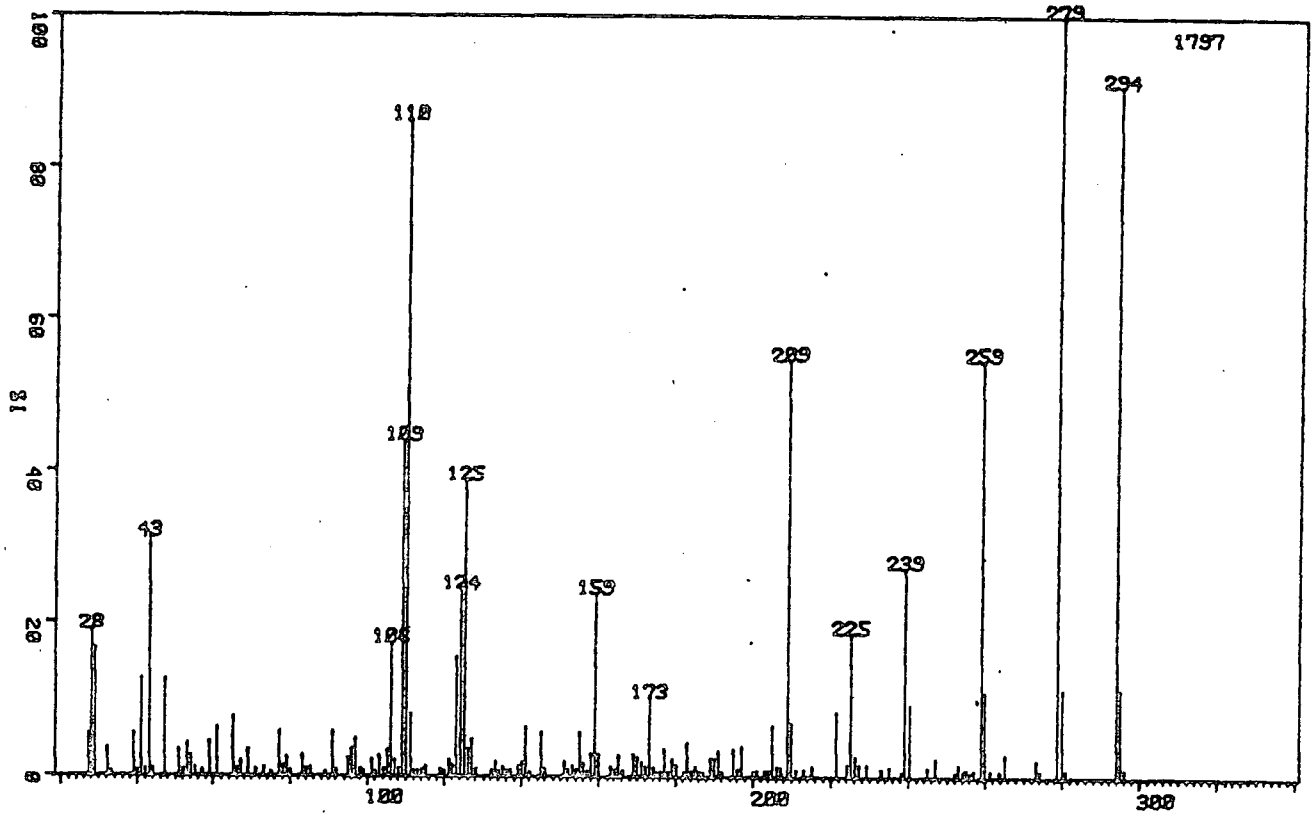


PEAK NO.	MASS	%HT. BASE
9	38.95	21.66*
10	39.85	6.72*
11	40.92	82.37*
12	42.02	3.91*
14	47.08	8.57*
15	48.05	0.37*
16	49.86	0.61*
20	54.10	5.45*
23	58.95	4.96*
26	62.00	0.39*
29	65.08	24.40*
30	66.07	6.64*
31	67.06	55.36*
32	67.19	1.93*
33	67.98	3.03*
39	75.04	0.76*
40	75.32	0.24*
44	78.93	9.87*
45	79.90	2.56*
48	83.01	2.88*
49	84.02	2.17*
50	85.03	2.88*
63	96.98	18.19*
64	97.97	4.37*
69	104.02	0.76*
70	105.04	22.54*
74	108.92	18.97*
89	124.92	100.00*
93	128.92	0.39*
95	132.92	1.34*
103	140.93	2.88*
104	141.96	0.37*
106	144.96	3.32*
122	164.97	3.88*
124	168.90	1.07*
147	204.96	8.91*
148	205.96	3.13*
149	206.90	1.37*
150	207.96	0.37*
151	208.93	4.37
159	224.99	4.18
160	225.98	0.63
161	226.93	1.44*
172	246.92	2.49*
173	247.91	0.46
174	252.92	0.93*
175	254.90	0.66*
176	258.87	4.47
177	259.93	0.73
178	260.95	0.45*
179	264.92	0.83
180	265.95	0.37
181	272.96	0.42
182	273.93	5.03*
183	274.90	1.27
184	276.99	0.24
185	278.84	17.02
186	279.76	3.30
187	293.93	14.58*
188	294.83	3.64*

NO. 17

MT159 S1 M.TAMURA
CAL: CALM28

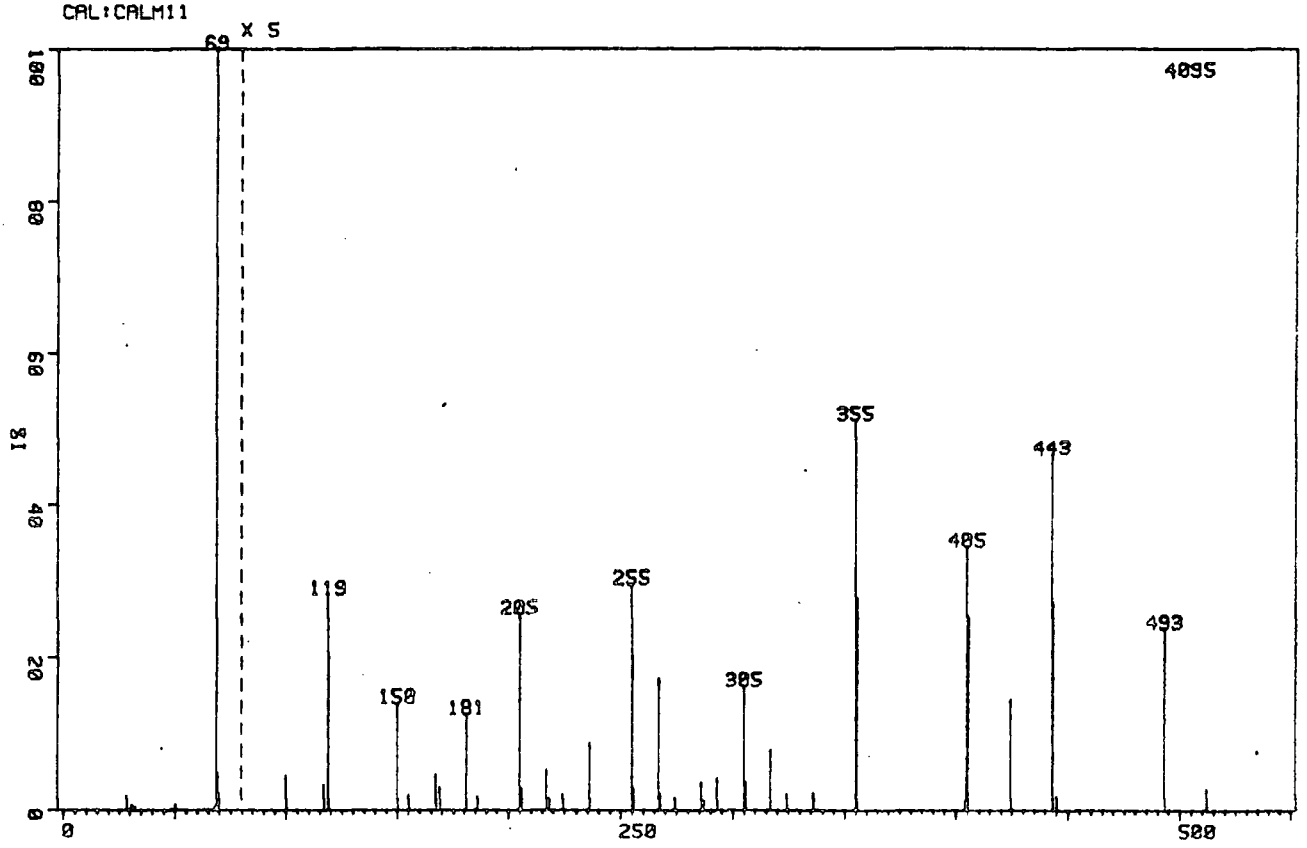
08-DEC-83



PEAK NO.	MASS	%HT. BASE						
6	38.95	5.56*	76	140.92	6.51*	151	258.89	54.59*
8	40.92	12.85*	79	145.96	1.00*	152	259.78	11.07*
9	42.02	0.95*	84	155.00	5.73*	158	278.63	100.00*
10	43.09	31.39*	88	158.91	23.87*	159	279.83	11.52*
19	58.95	4.51*	98	173.01	10.41*	160	280.91	0.99*
20	60.93	6.34*	99	174.02	1.17*	161	293.89	90.82*
21	65.05	7.74*	123	204.97	6.62*	162	294.96	11.52
22	66.06	0.95*	125	206.95	1.28*	163	296.05	1.11
28	77.01	5.79*	126	207.39	0.50*			
48	106.00	17.42*	127	208.85	54.70*			
50	108.00	1.11*	128	209.79	7.12*			
51	108.91	44.02*	132	221.32	8.46*			
52	109.86	86.20*	133	223.98	1.61*			
53	110.95	8.18*	134	225.01	18.70*			
62	123.00	15.69*	135	225.99	2.62			
63	124.01	24.43*	141	238.91	27.32*			
64	125.04	38.84*	142	240.25	9.40*			
66	126.97	4.84*						

NO. 18

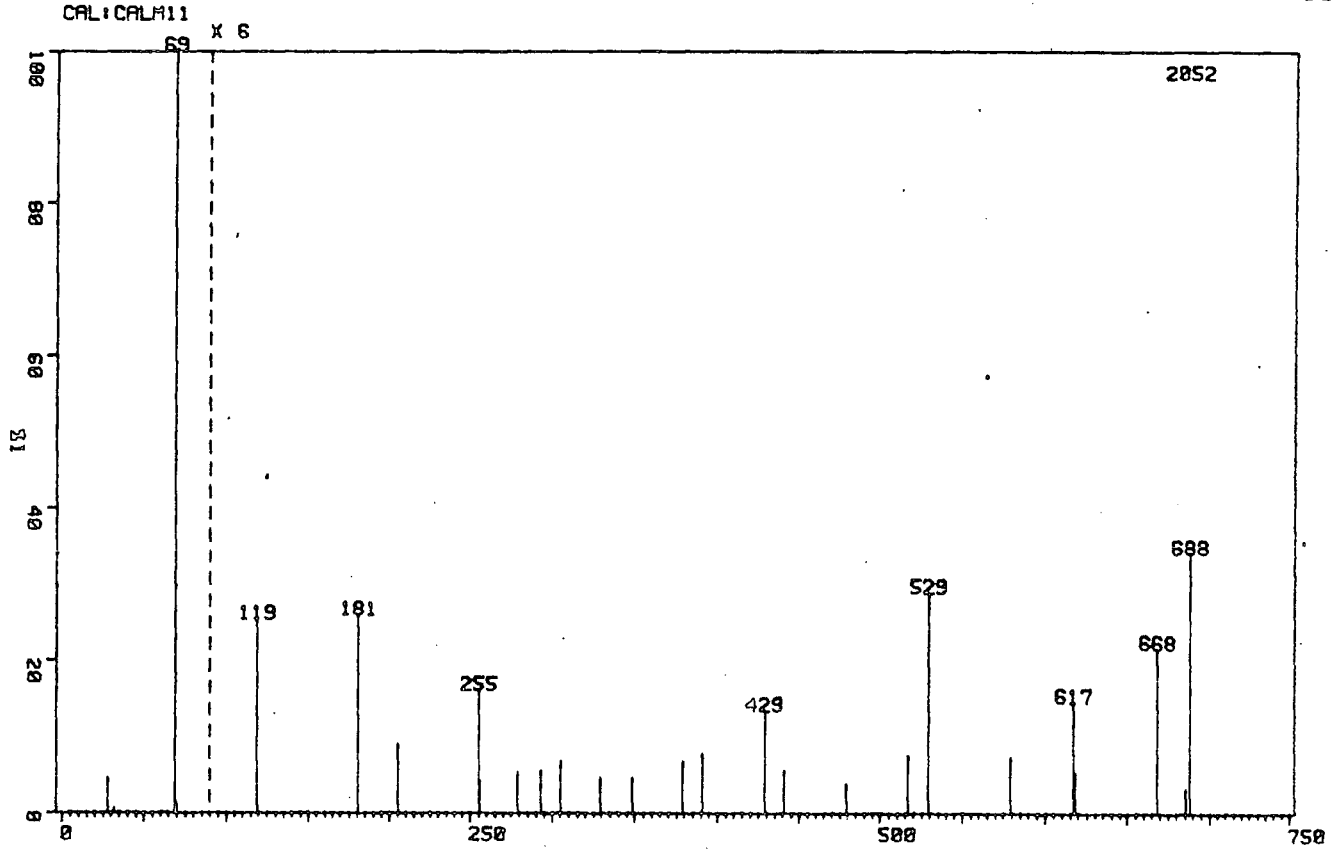
MT73 22 M.TAMURA 18-JAN-83
CAL:CALM11



PEAK NO.	M/E	%INT. BASE
1	28.14	1.90
2	30.93	0.73
3	32.03	0.46
4	49.88	0.71
5	67.75	0.97
6	68.12	0.46
7	68.36	0.11
8	69.17	100.00
9	69.19	4.96
10	69.33	0.51
11	69.49	0.61
12	69.69	0.36
13	69.89	2.22
14	99.90	0.90
15	117.04	0.46
16	118.95	5.67
17	119.07	1.08
18	149.92	2.53
19	154.04	0.69
20	167.05	0.13
21	168.97	0.61
22	180.94	2.03
23	181.02	0.32
24	203.97	5.15
25	204.22	0.49
26	204.99	0.56
27	216.97	1.07
28	218.01	0.51
29	223.00	0.42
30	230.98	1.28
31	254.95	0.93
32	255.32	9.05
33	255.87	0.56
34	266.95	3.44
35	267.92	0.42
36	274.00	0.36
37	285.96	0.71
38	287.19	0.27
39	292.93	0.45
40	304.91	3.27
41	305.87	0.51
42	317.93	0.36
43	318.93	0.13
44	354.94	15.00
45	355.91	1.53
46	367.91	0.36
47	404.88	6.13
48	405.85	1.53
49	417.90	0.36
50	442.87	11.00
51	443.84	1.53
52	455.84	0.36
53	492.82	6.13
54	493.79	1.53
55	505.79	0.36
56	530.77	0.36
57	531.74	0.13
58	543.74	0.13
59	580.72	0.13
60	581.69	0.13
61	593.69	0.13
62	618.67	0.13
63	619.64	0.13
64	631.64	0.13
65	668.62	0.13
66	669.59	0.13
67	681.59	0.13
68	706.57	0.13
69	707.54	0.13
70	719.54	0.13

NO. 19

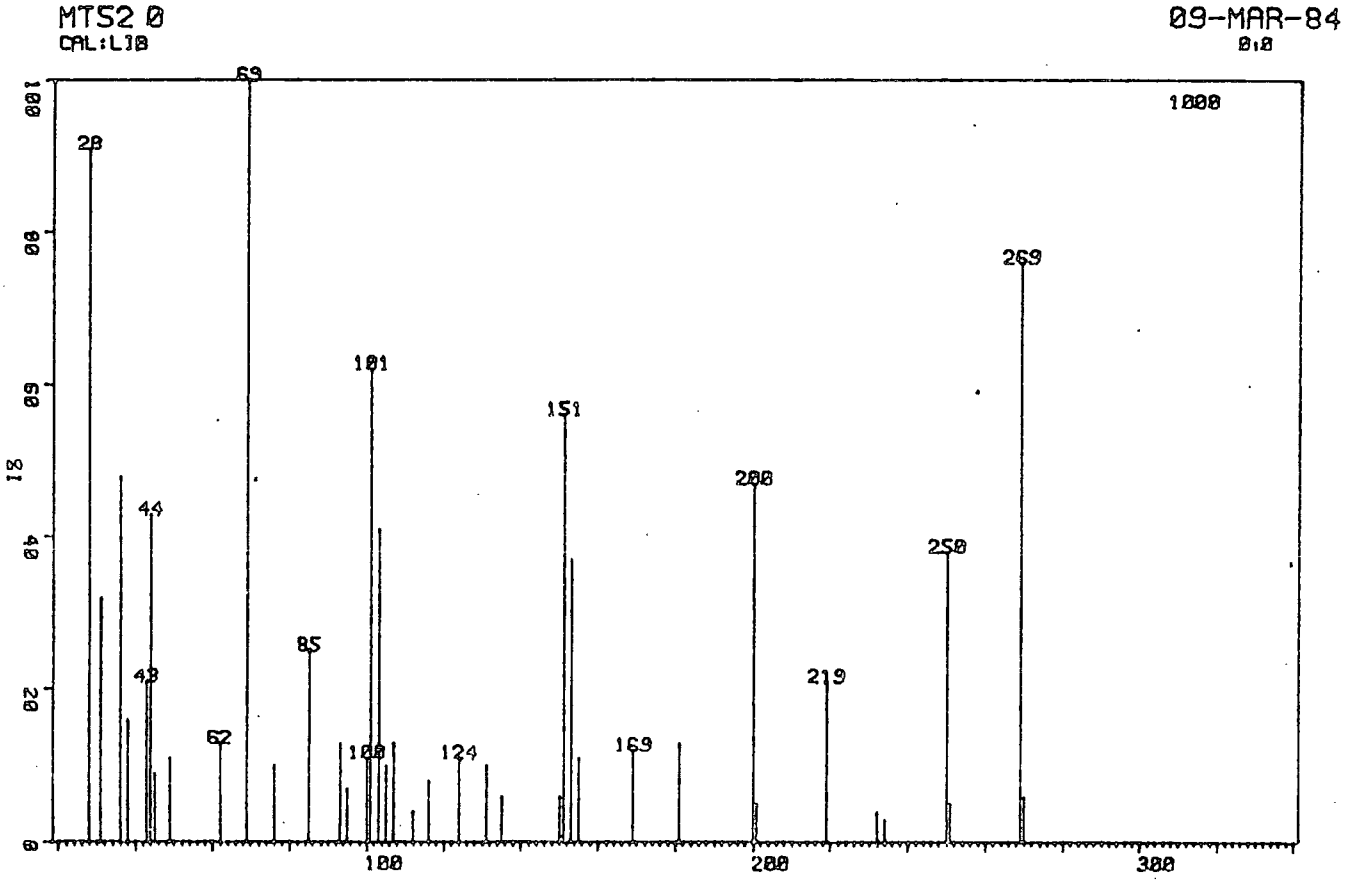
MT73 46 M.TAMURA 18-JAN-83
CAL:CALM11



PEAK NO.	MASS	%HT. BASE
1	28.14	4.33
2	32.02	0.56
3	40.45	0.73
4	48.43	0.83
5	50.98	10.00
6	69.35	1.12
7	82.91	1.61
8	118.97	4.24
9	180.84	4.34
10	204.93	1.51
11	254.97	2.68
12	256.08	0.68
13	273.93	0.80
14	352.88	0.93
15	404.94	1.12

16	32.03	0.46
17	348.17	0.72
18	378.22	1.19
19	420.87	1.02
20	429.99	4.34
21	441.00	0.93
22	470.05	0.63
23	516.95	1.27
24	529.07	7.83
25	579.18	1.91
26	614.81	1.44
27	618.24	0.89
28	668.03	5.41
29	688.53	9.58
30	690.10	5.76

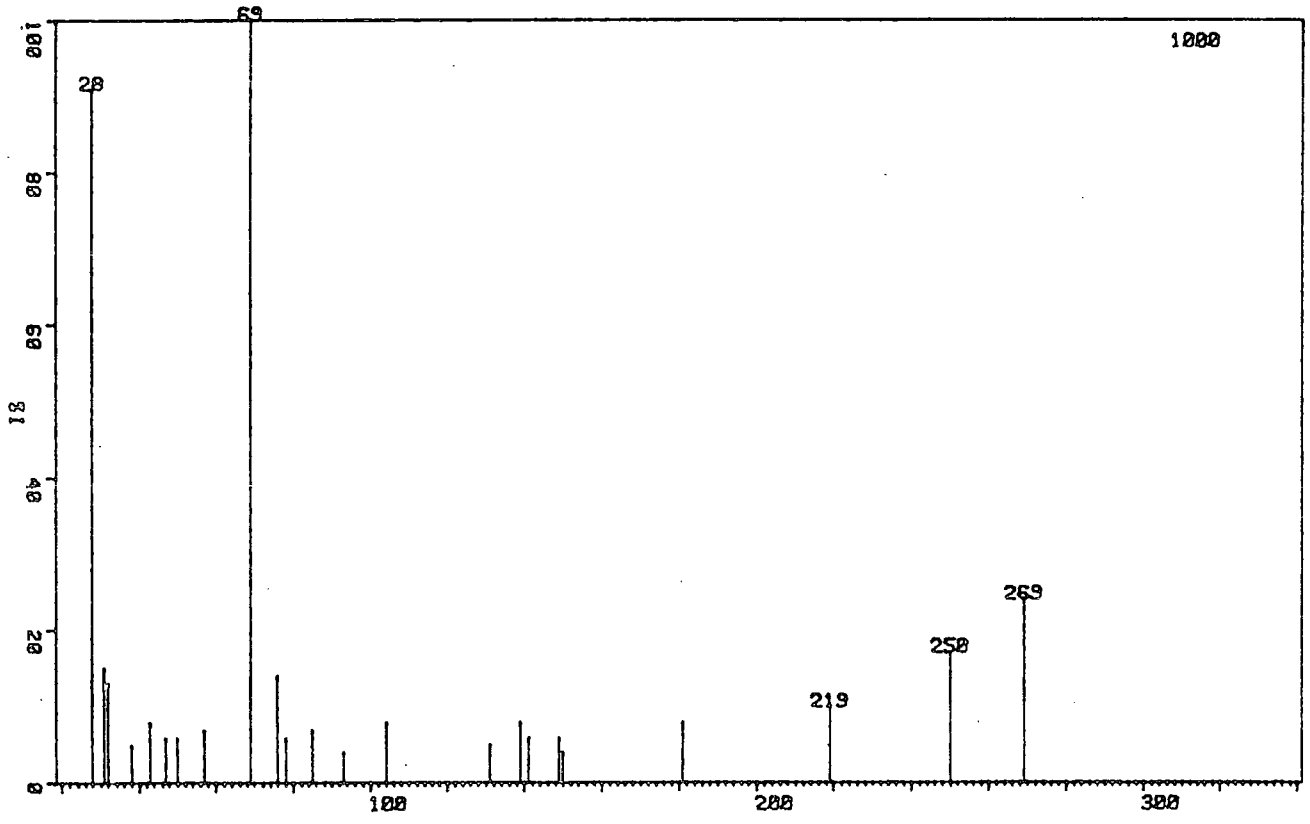
NO. 20



PEAK NO.	MASS	%HT. BASE						
1	26.30	3.36	40	85.01	25.00	75	150.02	6.06
2	27.23	9.01	41	86.07	3.38	76	150.92	56.31
3	28.12	90.99	42	87.00	7.88	77	152.04	4.73
4	29.00	4.73	43	88.03	4.95	78	152.97	17.14
5	30.90	32.66	44	92.03	5.18	79	155.04	10.59
6	32.01	9.91	45	93.05	12.84	80	169.06	11.71
7	35.16	5.41	46	94.08	3.15	83	181.10	12.84
8	36.15	47.97	47	95.10	7.21	84	183.15	6.08
9	38.06	15.54	50	99.95	11.04	85	192.06	4.28
10	41.00	8.11	51	100.92	61.94	86	199.97	47.30
11	42.08	4.73	52	102.98	41.22	89	219.09	20.95
12	43.14	20.72	53	105.06	10.14		232.13	4.28
13	44.15	43.24	54	107.06	13.06	91	244.11	1.35
18	49.01	10.59	64	124.12	10.59	9.	250.04	37.84
19	49.92	6.31	65	126.11	4.73	93	251.13	4.50
27	62.10	12.39	66	131.03	9.68	94	269.04	75.45
28	66.14	7.21	68	133.08	5.86	95	270.07	6.31
29	68.04	3.83	69	135.09	5.86			
30	68.99	100.00						

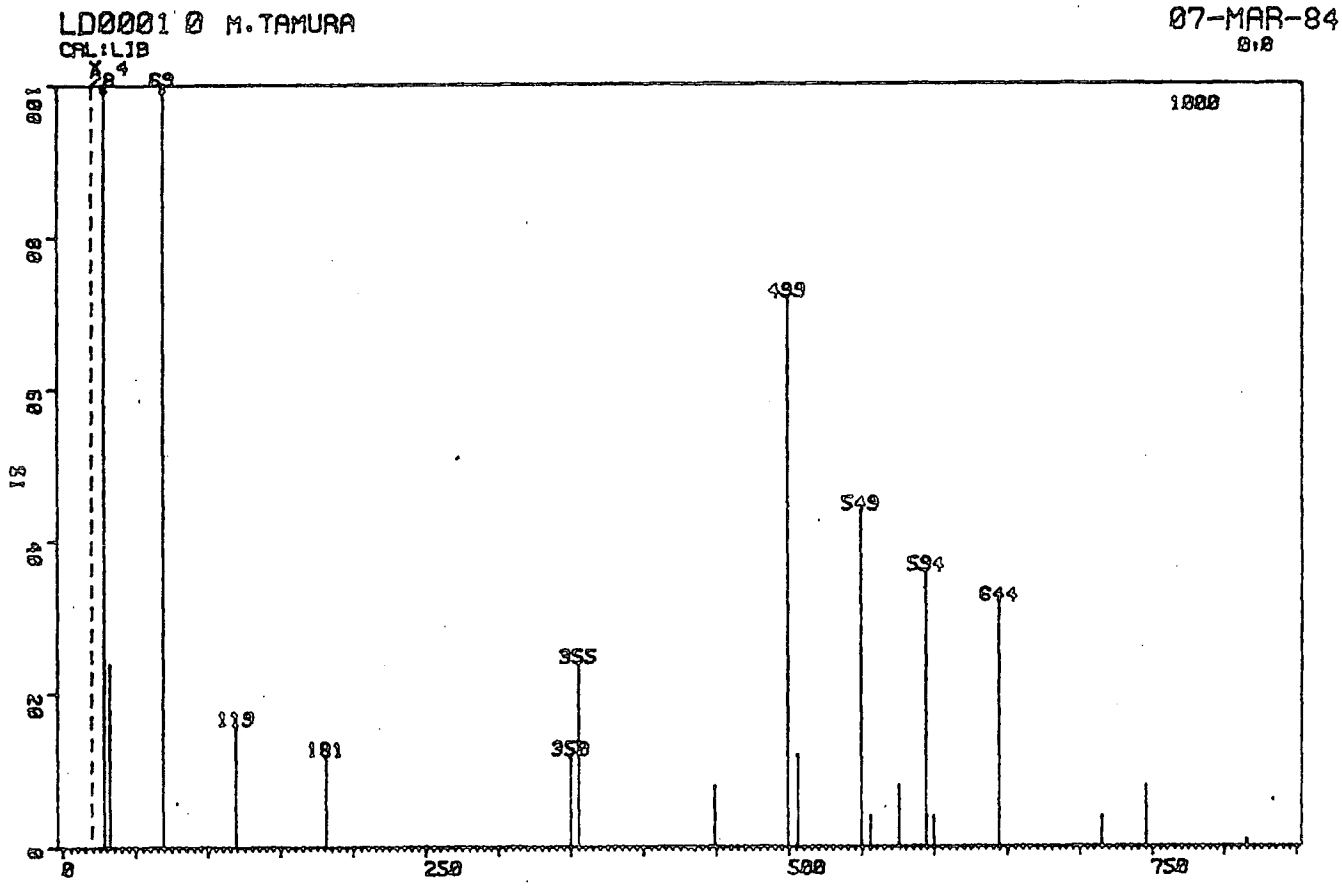
NO. 21

MTS320 0 M.TAMURA MTS3.20 23-FEB-84
CAL:L1B 0:0



PEAK NO.	MASS	%HT. BASE
1	28.14	90.91
2	30.91	14.72
3	32.02	12.58
4	38.07	5.19
5	43.12	7.79
6	47.05	6.06
7	49.87	5.63
8	57.13	7.36
9	68.95	100.00
10	76.03	14.29
11	77.94	6.49
12	84.98	6.93
13	92.99	4.33
14	103.43	6.93
15	130.81	5.19
16	138.83	9.23
17	140.84	5.06
18	148.99	6.06
19	149.84	8.33
20	180.90	8.79
21	199.86	40.74
22	218.89	14.69
23	249.90	14.88
24	268.76	24.81

NO. 22



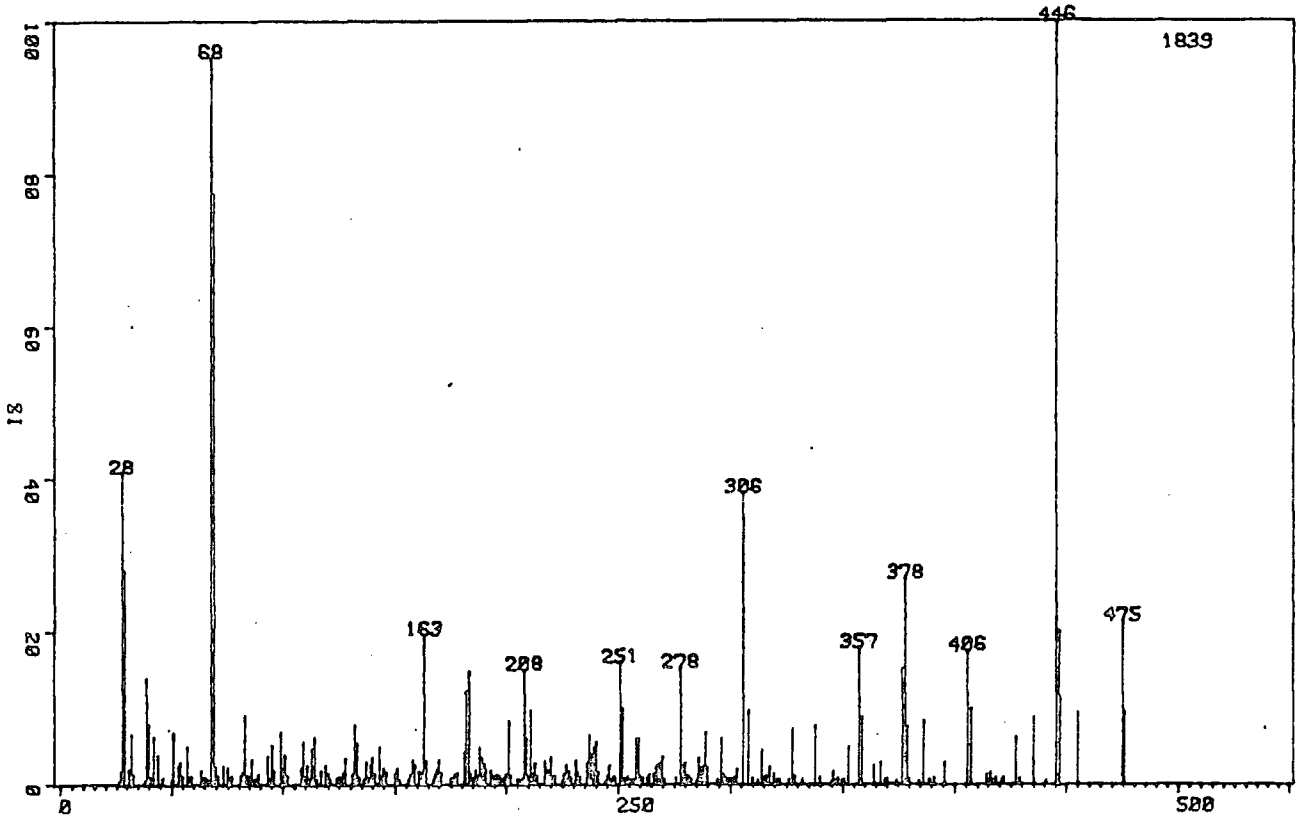
PEAK NO.	MASS	%HT. BASE			
1	28.06	38.55	21	354.67	5.72
2	28.96	1.17	22	361.66	1.31
3	31.94	5.72	23	399.60	1.38
4	44.07	3.72	24	430.46	1.24
5	68.92	100.00	25	449.37	2.00
6	69.84	0.97	26	456.41	0.97
7	84.99	1.17	27	461.45	1.03
8	118.86	3.59	28	482.37	0.97
9	130.87	0.83	29	499.37	18.14
10	142.92	1.17	30	506.34	2.76
11	168.83	1.24	31	549.22	11.38
12	175.92	1.17	32	556.08	0.83
13	180.84	2.69	33	575.09	1.59
14	254.78	0.83	34	594.18	0.90
15	261.81	0.90	35	599.09	1.03
16	266.81	1.03			
17	280.87	1.86	36	643.88	7.93
18	304.85	1.86	37	714.88	1.17
19	311.79	1.10	38	745.19	1.93
20	349.63	2.55			

NO. 23

MT144 65 M.TAMURA

CAL:CALM28

30-NOV-83

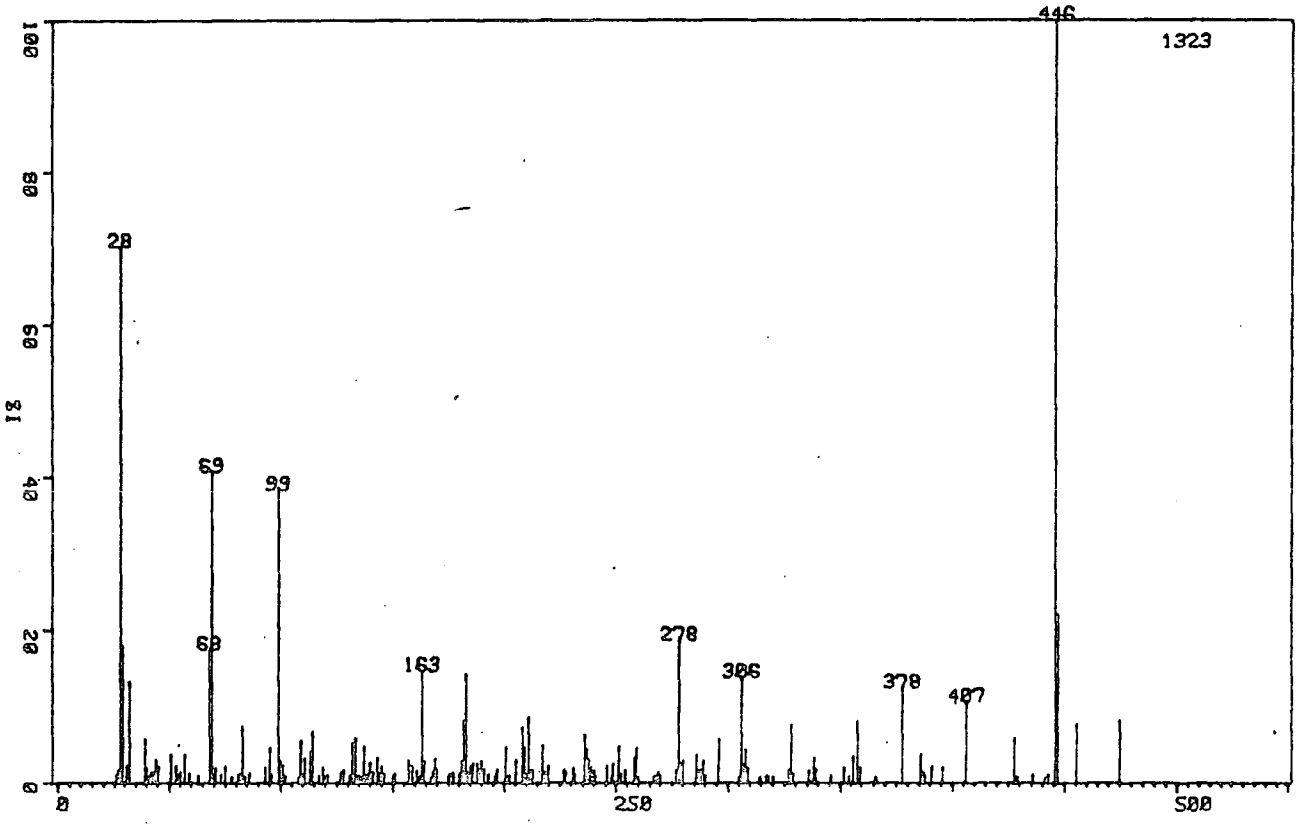


PEAK NO.	MASS	%HT. BASE
1	26.24	0.54
2	27.18	1.79
3	28.06	40.84
4	28.97	28.00
28	68.07	95.32
29	68.94	77.38
30	69.89	2.39
58	113.05	4.68
59	114.08	6.20
106	193.06	14.74
128	207.98	14.95
129	209.02	6.09
130	210.03	1.14
131	211.01	9.73
150	232.04	6.47
151	238.03	3.81
152	239.02	4.84
153	240.01	5.55
161	250.89	15.93
162	251.73	9.95
164	253.08	6.04
169	259.11	5.98
181	277.90	15.28
182	278.99	2.39
183	280.01	2.85
188	285.99	3.53
189	286.99	2.12
190	288.00	2.39
191	289.00	6.91
192	289.97	2.23
193	294.07	0.65
194	295.95	6.04
207	305.95	38.06
208	307.90	9.73
211	327.79	7.54
215	329.15	1.09
216	332.13	0.71
217	337.80	7.61
225	352.64	4.95
226	357.19	17.09
227	358.74	8.14
228	376.78	15.06
229	377.96	26.92
240	378.96	1.45
242	405.71	17.46
243	407.45	9.95
251	427.37	6.14
252	429.05	0.82
253	435.14	6.75
254	441.30	0.54
255	445.76	100.00
256	446.82	19.96
257	447.59	11.32
258	455.26	2.30
259	474.03	21.82
260	475.94	9.22

NO. 24

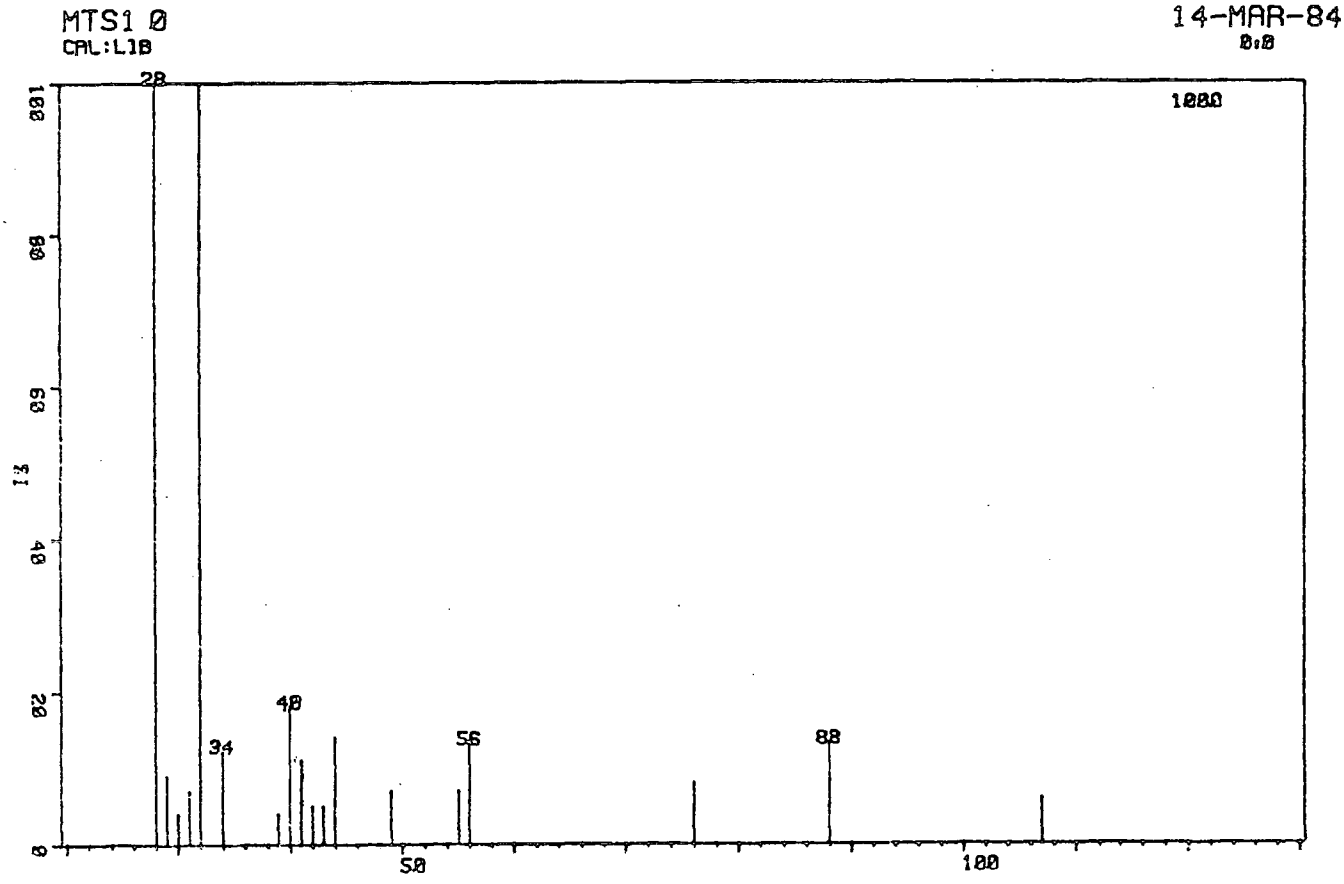
MT144 77 M.TAMURA
CAL:CALM28

30-NOV-83



PEAK NO.	MASS	%HT. BASE
1	26.23	1.04
2	27.18	1.74
3	28.06	70.22
4	28.93	17.84
5	30.84	2.34
6	31.94	13.23
7	38.06	5.82
21	68.08	17.46
22	68.99	40.67
36	98.99	38.32
37	99.93	2.80
38	100.99	2.34
53	132.06	5.22
54	133.08	5.97
74	163.03	14.66
75	164.04	2.80
85	181.00	2.80
86	182.03	8.24
87	183.02	14.21
100	205.10	3.02
101	207.98	7.33
102	208.99	4.61
103	209.93	1.13
104	210.98	8.62
115	236.02	6.35
116	237.01	4.46
117	238.00	3.17
127	258.02	3.25
128	259.00	4.61
135	278.06	18.67
136	279.03	2.57
145	306.02	13.93
146	307.05	2.37
147	308.07	4.46
153	327.07	1.66
154	328.05	7.53
162	356.04	3.55
163	357.94	8.16
166	377.68	12.47
167	386.05	3.95
174	406.61	10.66
175	407.65	5.70
176	445.91	100.00
177	446.99	22.07
178	455.90	2.79
182	475.15	8.24

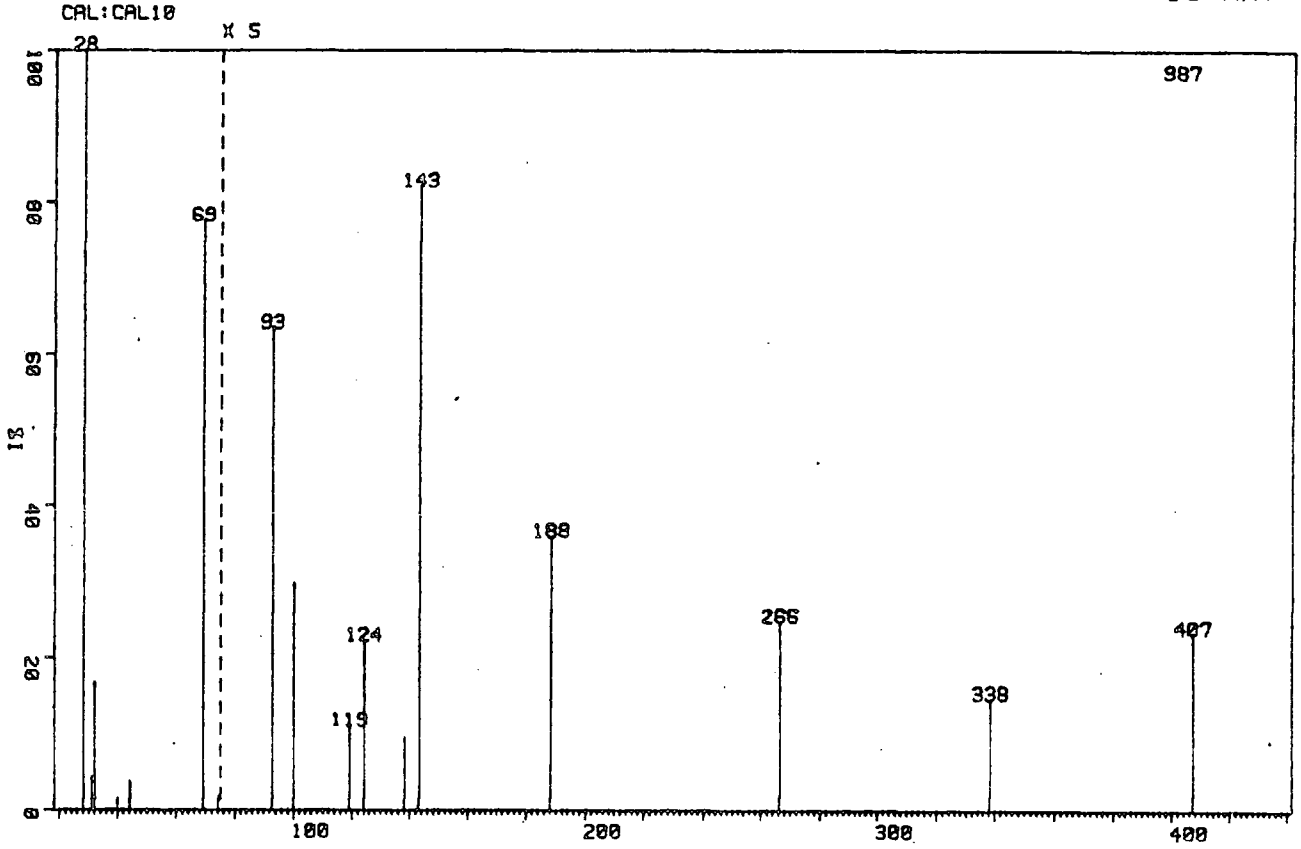
NO. 25



peak No.	mass	%ht base
1	28.11	100
2	28.99	8.64
3	29.82	0.42
4	30.91	0.71
5	32.01	100
6	34.17	1.15
7	39.03	0.42
8	39.86	1.74
9	41.02	1.05
10	42.12	0.51
11	43.15	0.51
12	44.15	13.55
13	49.01	0.63
14	55.25	0.63
15	56.25	1.27
16	76.18	0.73
17	88.19	1.25
18	107.12	0.61

NO. 26

MTS3R 20 M.TAMURA 10-MAY-83
CAL:CAL10

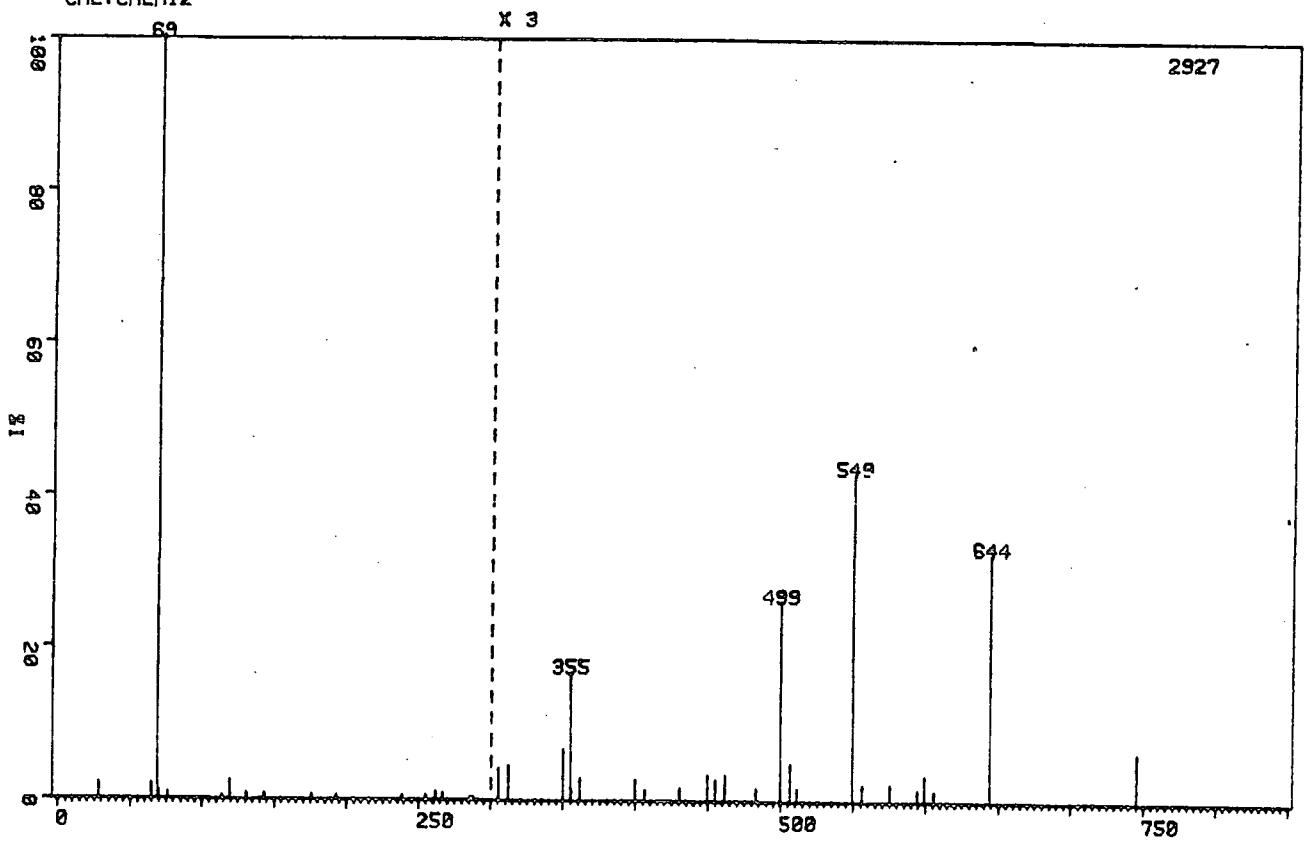


PEAK NO.	MASS	%HT. BASE
1	28.13	100.00
2	30.92	4.36
3	32.03	16.72
4	39.86	1.52
5	44.16	3.85
6	69.05	77.51
7	74.17	1.93
8	93.10	12.66
9	100.00	5.98
10	119.10	2.23
11	124.12	4.46
12	138.12	1.93
13	143.06	16.41
14	188.17	7.19
15	266.27	4.96
16	338.32	2.94
17	407.20	4.66

NO. 27

MT118 37 M.TAMURA
CAL:CALM12

26-OCT-83



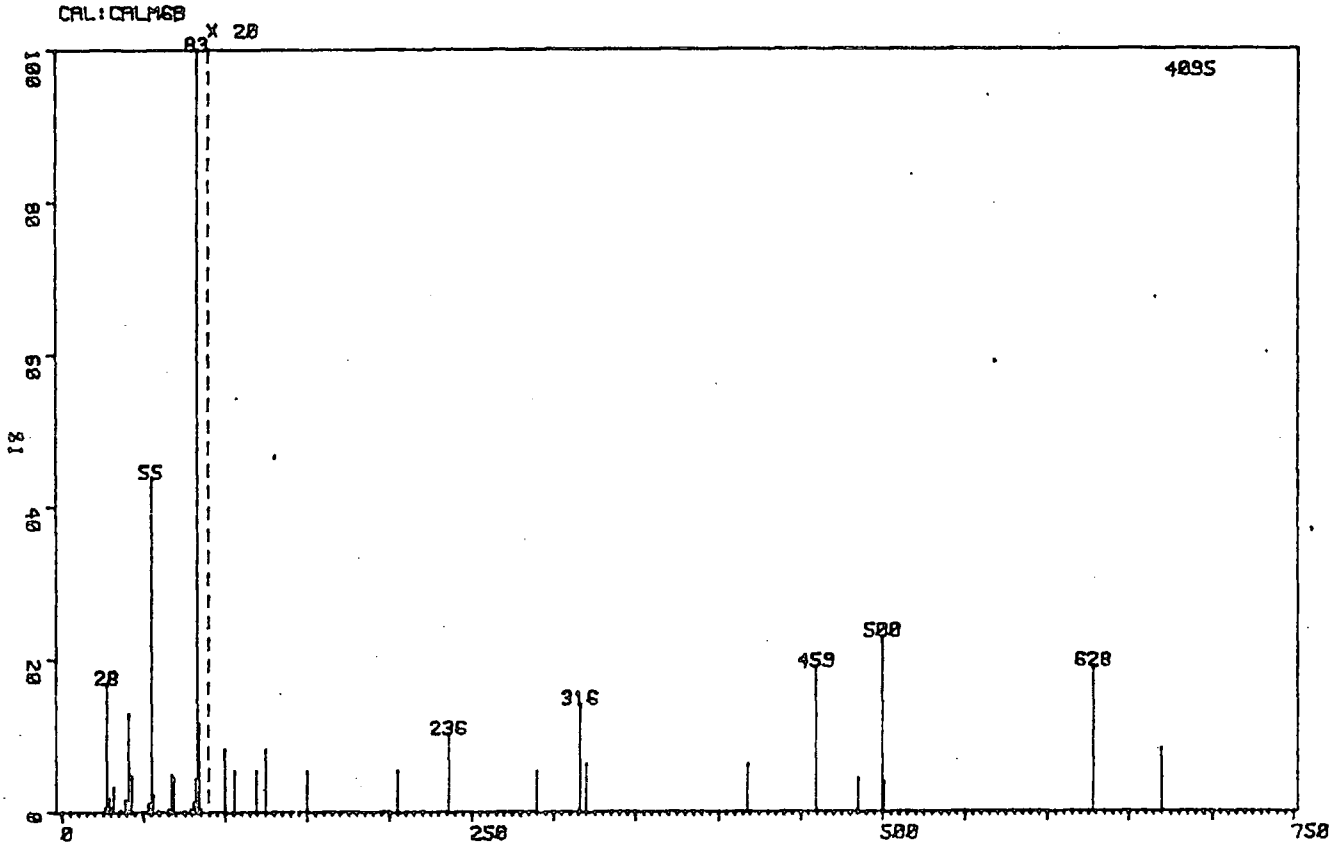
PEAK NO.	MASS	%HT. BASE
1	28.06	2.12
2	64.40	2.05
3	68.92	100.00
4	69.87	1.13
5	76.04	0.92
6	113.92	0.55
7	118.87	2.53
8	130.86	0.79
9	142.91	0.85
10	175.90	0.65
11	192.82	0.61
12	237.83	0.58
13	254.76	0.68
14	261.88	1.16
15	266.88	0.99
16	285.81	0.44
17	287.73	0.48
18	304.82	1.37
19	311.74	1.50
20	349.64	2.22
21	354.61	5.57
22	355.68	0.51
23	361.61	0.99
24	399.54	0.92
25	406.55	0.48
27	430.56	0.55
28	449.39	1.13
29	455.08	0.92
30	461.47	1.13
31	482.47	0.58
32	499.32	8.71
33	506.37	1.64
34	511.25	0.58
35	549.10	14.31
36	556.13	0.75
37	575.19	0.75
38	594.15	0.51
39	599.13	1.13
40	606.01	0.48
41	643.91	10.83
42	745.36	2.15

NO. 28

MT171 10 M.TAMURA

06-JAN-84

CAL:CALM6B



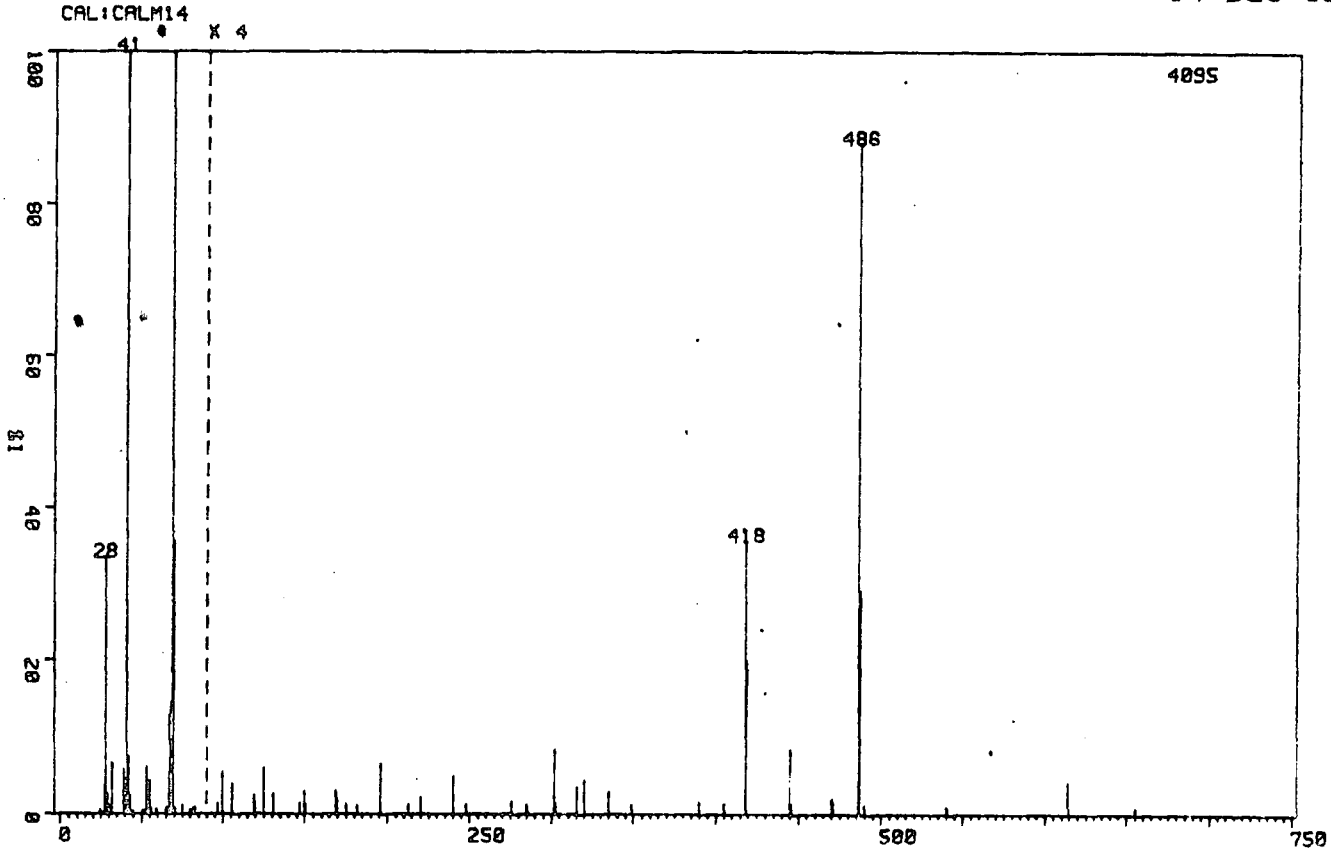
PEAK NO.	MASS	%HT. BASE
1	27.18	0.66
2	28.07	16.90
3	28.96	1.88
4	30.85	0.61
5	31.95	3.32
6	36.64	0.29
7	36.85	0.22
8	38.97	1.61
9	39.84	0.49
10	40.96	13.02
11	42.05	1.49
12	43.12	4.74
13	50.94	0.22
14	53.11	1.07
15	54.15	1.25
16	55.16	43.91
17	56.15	2.37
18	59.04	0.27
19	65.15	0.49
20	67.13	4.93
21	68.08	0.83
22	68.97	4.64
23	75.08	0.32
24	79.03	0.46
25	81.02	1.44
26	82.09	4.54
27	83.11	100.00
28	84.11	11.84
29	85.09	0.39
30	99.88	0.42
31	106.02	0.27
32	118.96	0.27
33	125.03	0.42
34	149.94	0.27
35	205.07	0.27
36	236.10	0.51
37	290.18	0.27
38	316.23	0.71
39	320.04	0.32
40	418.11	0.32
41	459.31	0.95
42	485.41	0.22
43	500.31	1.15
44	501.36	0.20
45	628.40	0.95
46	669.30	0.42

NO. 29

MT160 67 M.TAMURA

CAL:CALM14

14-DEC-83



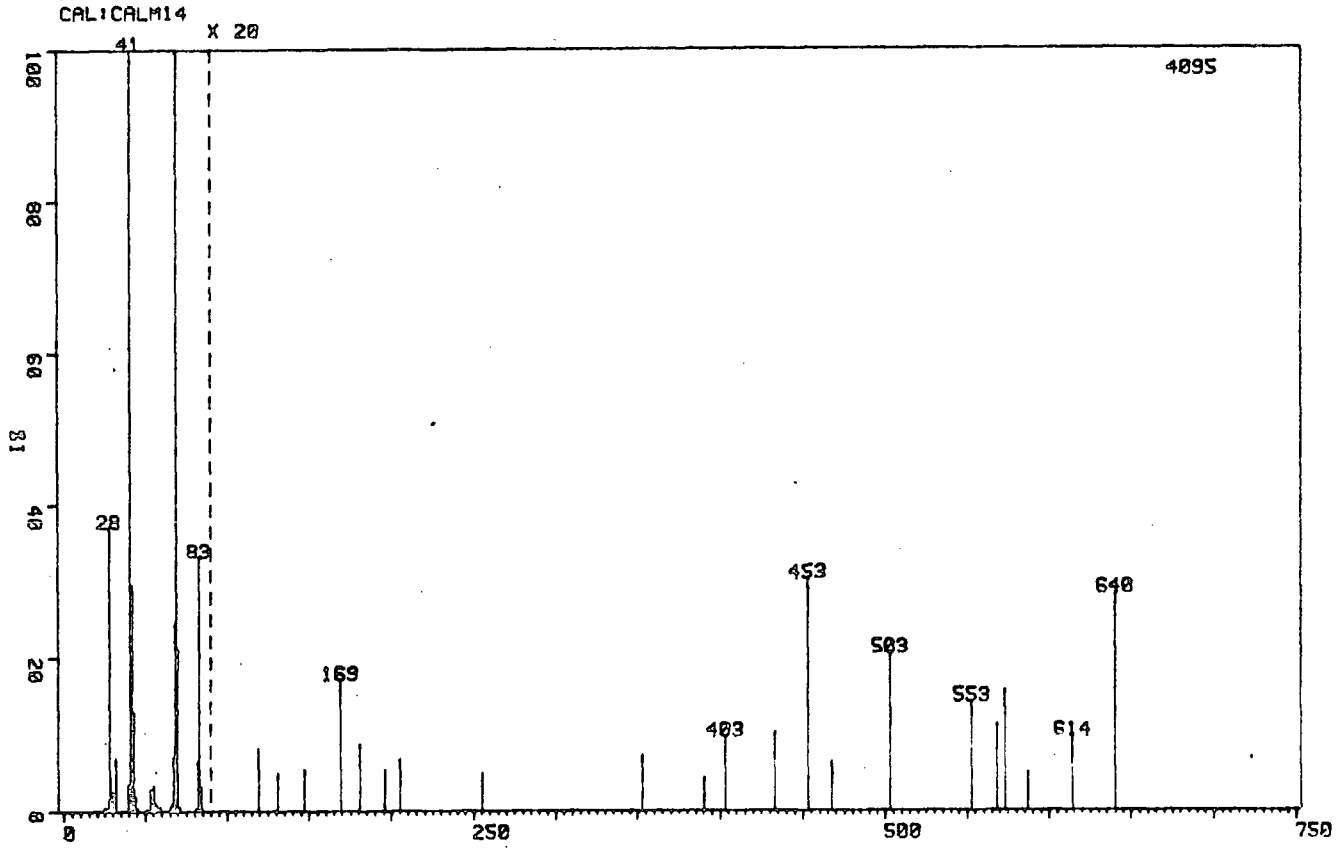
PEAK NO.	MASS	%HT. BASE
1	24.57	0.22
2	24.75	0.56
3	24.97	0.27
4	27.25	3.49
5	28.13	43.50
6	29.02	2.61
7	30.92	1.20
8	32.01	6.57
9	39.00	5.67*
10	39.88	2.42*
11	40.99	100.00*
12	42.08	7.42
13	43.15	1.42
18	53.12	6.18
19	54.15	2.93*
20	55.15	4.25*
25	67.06	12.97*
26	67.16	5.01*
27	67.48	0.24*
28	68.00	14.60
29	68.93	100.00*
30	69.83	35.56*
31	71.00	0.76
32	75.04	1.05
38	99.89	1.34
39	106.05	0.98
40	118.96	0.41*
41	119.95	0.39
42	125.04	1.49*
51	195.98	1.61
52	213.01	0.32
53	219.96	0.54
54	239.96	1.25
58	302.00	2.12*
59	303.02	0.77*
60	31[illegible].03	[illegible].21
61	319.9[illegible]	1.13
66	417.91	8.51
67	418.66	4.90
68	444.75	0.17
69	445.97	0.20
70	470.10	0.51*
71	[illegible]	[illegible]
72	[illegible]	[illegible]
73	487.06	[illegible]
74	4[illegible]	[illegible]
75	5[illegible]	[illegible]
76	514.04	1.[illegible]
77	535.13	0.22

NO. 30

MT160 93 M.TAMURA

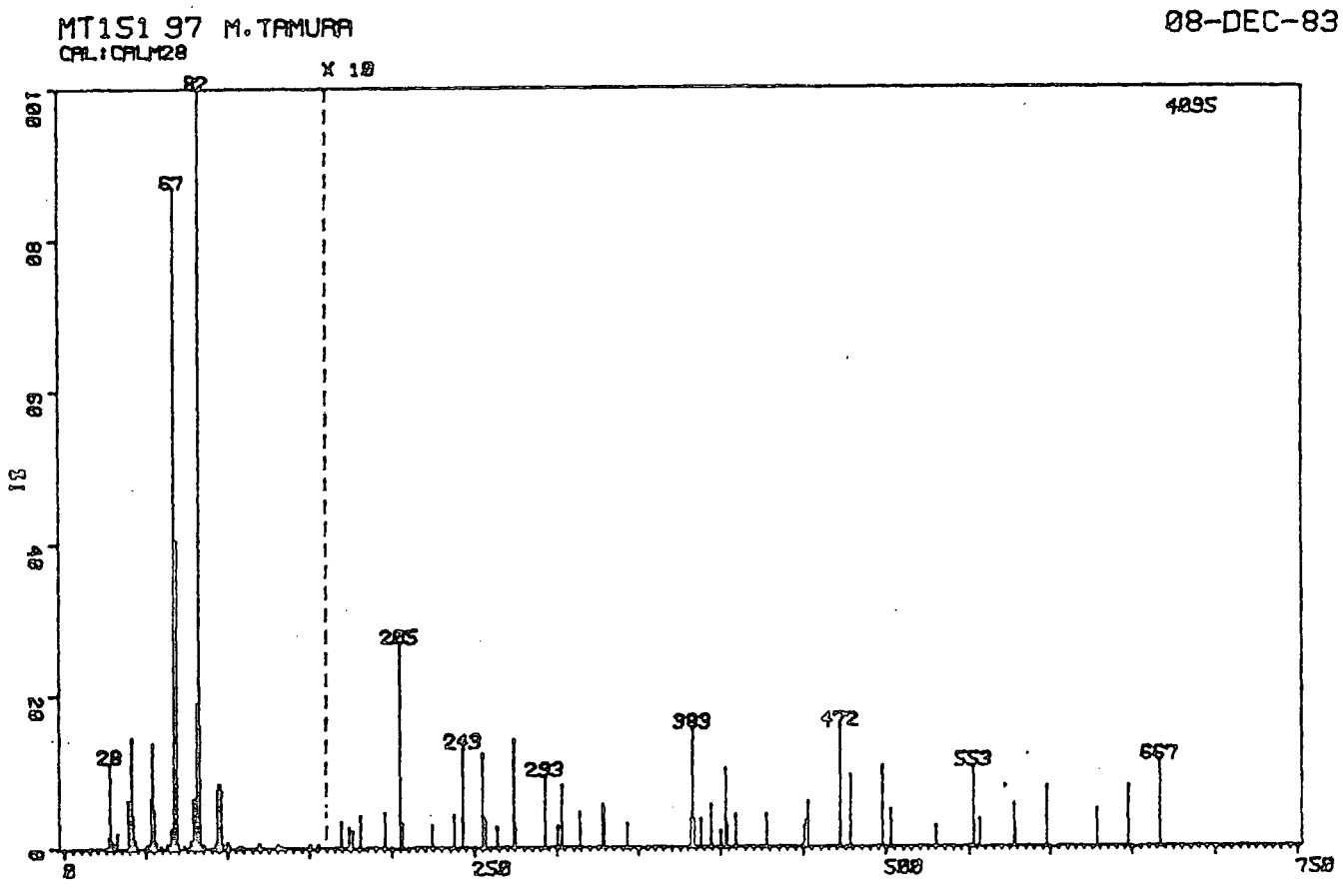
CAL:CALM14

14-DEC-83



PEAK NO.	MASS	%HT. BASE						
1	24.70	0.37	21	54.14	1.76*	41	140.96	0.[illegible]
2	24.75	0.37	22	55.16	3.30	42	142.93	0.[illegible]
3	24.79	0.27	23	56.17	1.10*	43	180.97	[illegible]
4	24.84	0.44	24	57.16	0.76	44	[illegible]	[illegible]
5	27.25	1.54	25	59.03	0.56	45	203.78	0.[illegible]
6	28.13	37.02	26	65.16	0.63*	46	254.[illegible]	[illegible]
7	29.02	2.44	27	66.13	1.00	47	402.95	[illegible]
8	29.85	2.52	28	67.07	7.20	48	389.9[illegible]	[illegible]
9	30.92	1.20	29	68.03	24.5?*	49	403.06	[illegible]
10	32.01	6.86	30	68.98	100.00*	50	432.[illegible]	[illegible]
11	39.00	3.54	31	69.61	0.3[illegible]	51	452.[illegible]	[illegible]
12	39.88	1.78	32	69.93	21.1[illegible]	52	467.15	[illegible]
13	40.73	0.22*	33	70.99	0.51	53	502.[illegible]	[illegible]
14	40.99	100.00*	34	80.95	0.37	54	509.87	[illegible]
15	42.07	29.45	35	82.03	3.47*	55	567.[illegible]	[illegible]
16	43.14	12.09	36	83.05	33.19*	56	572.[illegible]	[illegible]
17	44.17	1.93*	37	84.08	3.[illegible]*	57	686.[illegible]	[illegible]
18	45.19	0.42*	38	85.01	[illegible]	58	[illegible]	[illegible]
19	50.97	0.34*	39	118.92	0.4[illegible]	59	830.[illegible]	[illegible]
20	53.12	2.81	40	130.93	0.34*			

NO. 31

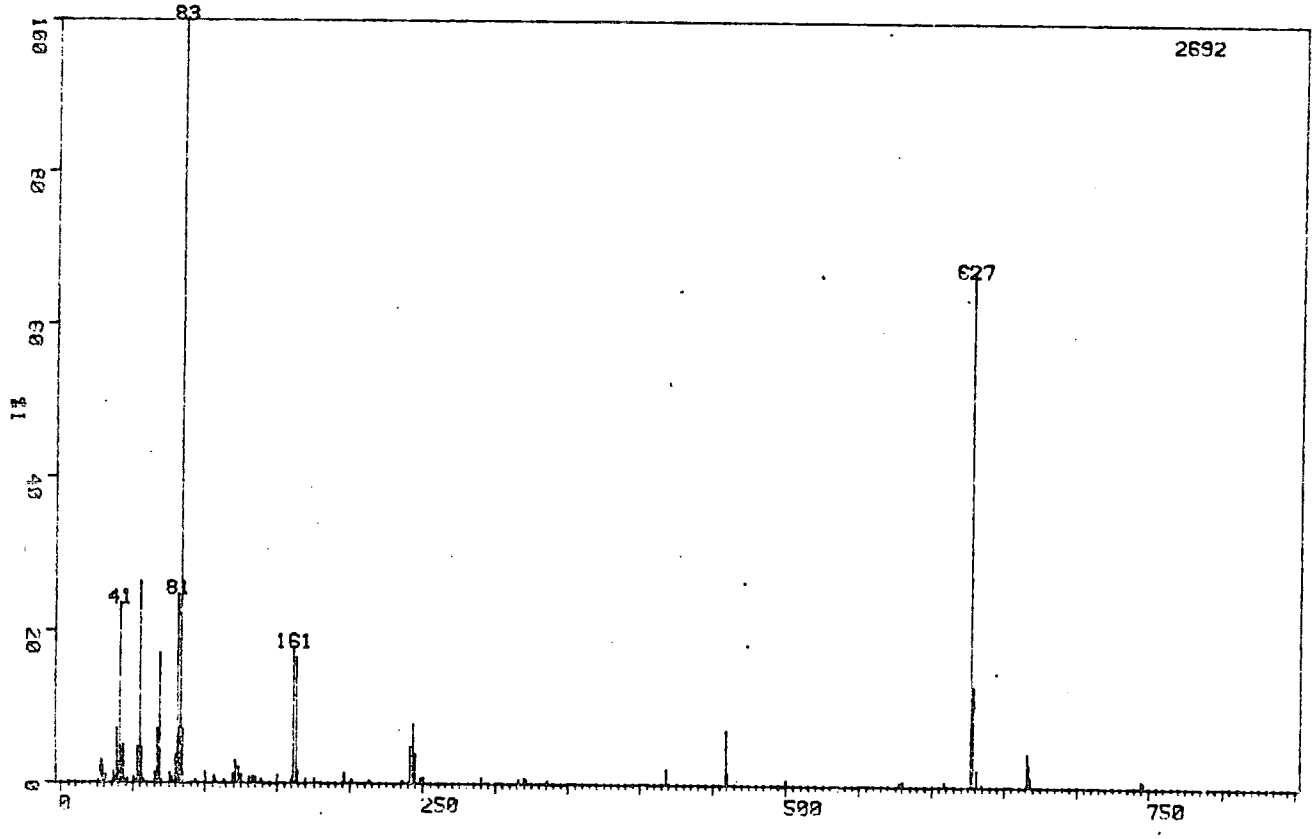


peak No.	mass	%ht base			
7	38.95	6.28	94	452.677	0.61
10	42.03	4.42	97	497.47	1.07
26	67.05	86.89	99	529.63	0.27
27	68.02	6.23	100	552.72	1.07
29	68.91	40.53	101	556.74	0.37
37	78.99	6.57	103	578.87	0.22
38	80.97	18.97	104	597.80	0.81
39	82.02	100.00	105	627.98	0.49
40	82.96	16.12	106	647.95	0.21
45	94.04	7.74	107	667.12	1.10
64	204.90	2.69			
68	242.85	1.32			
73	273.87	1.42			
88	402.91	1.05			

NO. 32

MT190 12 M.TAMURA
CAL:CALM1S

15-MAR-84



PEAK NO.	MASS	%HT. BASE
1	26.30	0.48
2	27.23	2.13
3	28.12	2.93
4	29.01	2.19
5	30.89	1.09
6	33.78	0.17
10	[illegible]	[illegible]
11	[illegible]	[illegible]
12	42.06	4.09
13	43.17	3.67
19	53.09	4.64
20	54.13	2.86
21	55.15	26.23
22	56.14	4.53
26	67.04	0.13
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]

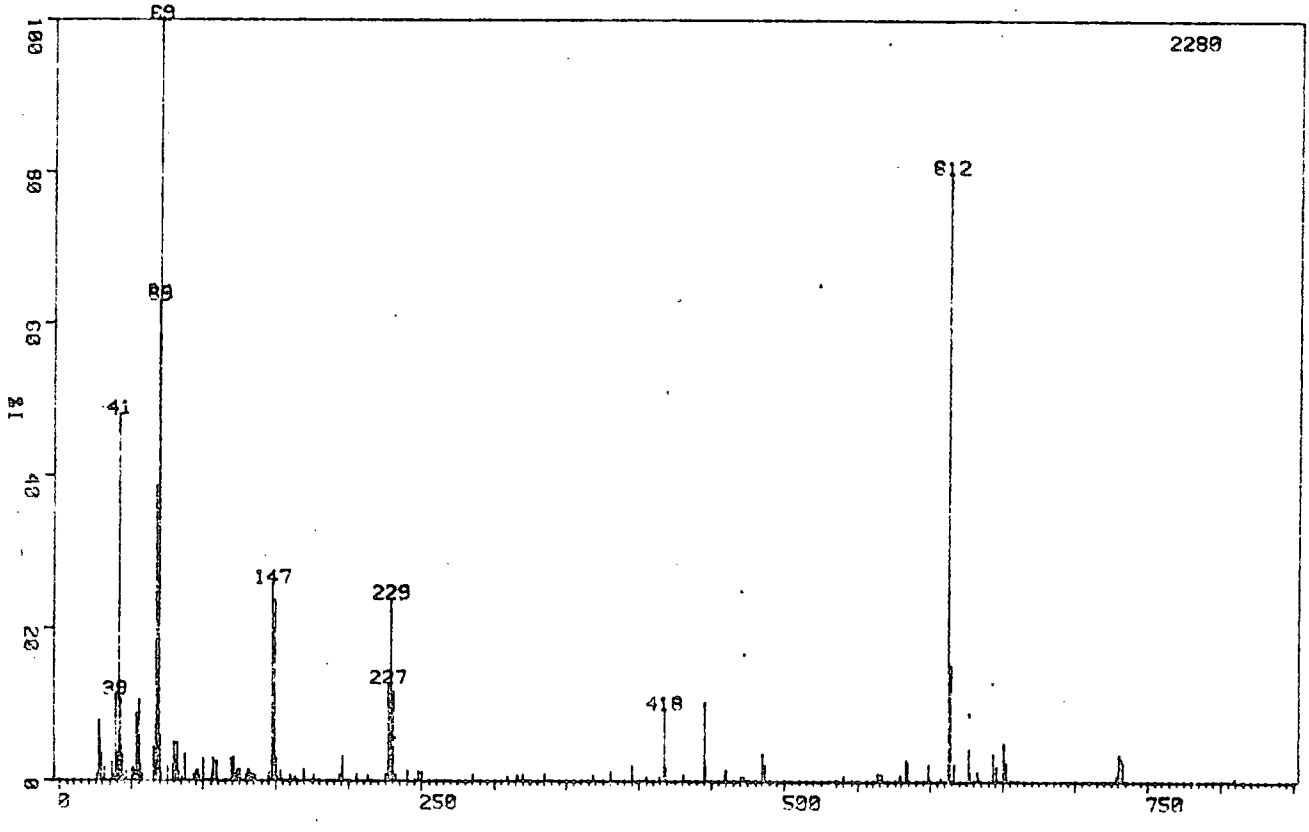
36	81.90	4.49
37	82.09	7.84
38	83.12	100.00
39	84.09	6.95
46	119.74	1.13
47	119.96	0.59
48	120.22	2.93
49	122.98	2.04
50	125.04	1.08
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
68	246.05	7.75
69	344.91	3.83
71	250.12	0.82
72	290.26	0.74
73	316.26	0.52
74	320.20	0.79
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]

[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
84	628.86	66.68
85	629.12	13.11
86	630.73	1.15
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]
91	[illegible]	[illegible]
[illegible]	[illegible]	[illegible]

NO. 33

MT191 7 M.TAMURA
CAL:CALM1S

15-MAR-84

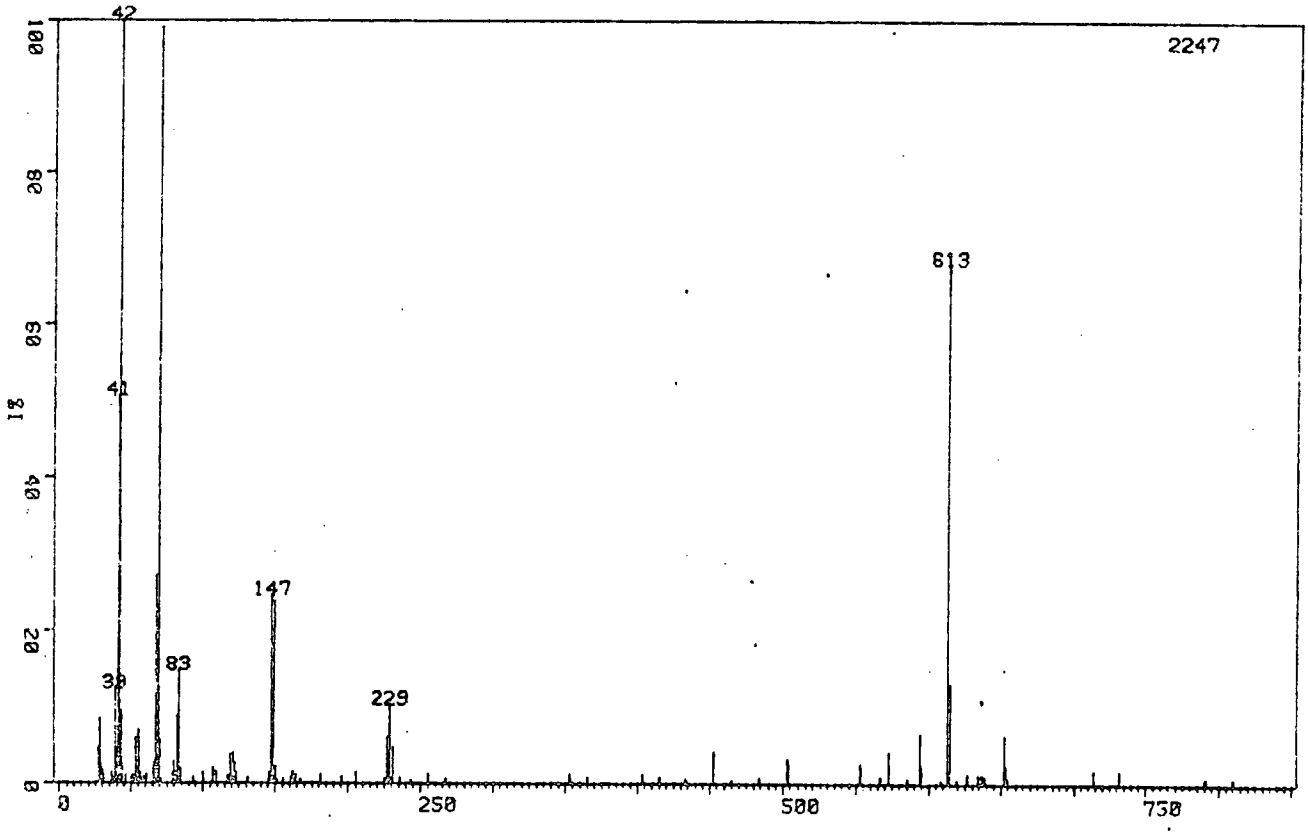


PEAK NO.	MASS	INT. BASE					
1	26.30	0.79	33	71.85	2.62		
2	27.23	7.81	34	74.83	6.50		
3	28.12	9.48	35	77.92	5.48		
4	32.[illegible]	2.42	36	81.00	2.63		
5	38.95	11.23	37	81.95	4.91		
6	39.88	5.51	38	83.[illegible]	[illegible]		
7	40.[illegible]	29.07	39	106.75	2.98		
8	42.[illegible]	10.78	40	107.61	2.53		
9	43.[illegible]	3.29	41	110.74	3.51		
10	44.[illegible]	2.[illegible]	42	111.[illegible]	[illegible]		
11	45.[illegible]	[illegible]	43	112.[illegible]	[illegible]		
12	46.[illegible]	[illegible]	44	113.[illegible]	[illegible]		
13	47.[illegible]	[illegible]

NO. 34

MT192 S M.TAMURA
CAL:CAL14A

14-MAR-84



PEAK NO.	MASS	INT. PAS.						
1	27.23	4.53	44	118.10	3.68			
2	28.12	8.41	45	119.87	2.58			
8	38.98	12.47	46					
9	39.97	4.36						
10	40.95	50.73						
11	42.04	100.00						
12	43.11	9.39						

COLLOQUIA AND CONFERENCES

COLLOQUIA AND CONFERENCES

The Board of Studies in Chemistry requires that each research thesis contains an appendix listing:

(A) all research colloquia, research seminars and lectures arranged by the Department of Chemistry and the Durham University Chemical Society during the period of the writer's residence;

(B) all research conferences attended and papers presented by the writer of the thesis, during the period when the research for the thesis was carried out.

(A) RESEARCH COLLOQUIA, SEMINARS AND LECTURES

Durham University Chemistry Department Colloquia

1982

20 January — Dr. M.R. Bryce (University of Durham), "Organic metals".

27 January — Dr. D.L.H. Williams (University of Durham), "Nitrosation and nitrosoamines".

3 February — Dr. D. Parker (University of Durham), "Modern methods of determining enantiomeric purity".

10 February — Dr. D. Pethrick (University of Strathclyde), "Conformation of small and large molecules".

17 February — Prof. D.T. Clark (University of Durham), "Plasma Polymerization".

24 February — Prof. R.D. Chambers (University of Durham), "Recent reactions of fluorinated internal olefins".

2 March — Dr. L. Field (University of Oxford), "Applications of N.M.R. to biosynthetic studies on penicillin".

3 March — Dr. P. Bamfield (I.C.I. Organics Division), "Computer aided design in synthetic organic chemistry".

17 March	Prof. R.J. Haines (University of Natal), "Clustering around Ruthenium, Iron and Rhodium".
7 April	Dr. A. Pensak (DuPont, U.S.A.), "Computer aided synthesis".
5 May	Dr. G. Tennant (University of Edinburgh), "Exploitation of the aromatic nitro-group in the design of new heterocyclisation reactions".
7 May	Dr. C.D. Garner (University of Manchester), "The structure and function of Molybdenum centres in enzymes".
26 May	Dr. A. Welch, (University of Edinburgh), "Conformation patterns and distortion in carbometalloboranes".
14 June	Prof. C.M.J. Stirling (University College of Wales, Bangor), "How much does strain affect reactivity?"
28 June	Prof. D.J. Burton (University of Iowa, U.S.A.), "Some aspects of the chemistry of fluorinated phosphonium salts and their phosphonates".
2 July	Prof. H.F. Koch (Ithaca College, University of Cornell, U.S.A.), "Proton transfer to and elimination reactions from localized and delocalized carbanions".
13 September	Prof. R. Neidlein (University of Heidelberg, FRG), "New aspects and results of bridged annulene chemistry".
27 September	Dr. W.K. Ford (Xerox Research Center, Webster, N.Y.), "The dependence of the electron structure of polymers on their molecular architecture".
13 October	Dr. W.J. Feast (University of Durham), "Approaches to the synthesis of conjugated polymers".

14 October — Prof. H. Suhr (University of Tubingen, FRG), "Preparative Chemistry in Non-equilibrium plasmas".

27 October — Dr. C.E. Housecroft (Oxford High School/Notre Dame University) "Bonding capabilities of butterfly-shaped Fe_4 units implications for C-H bond activation in hydrocarbon complexes".

28 October — Prof. M.F. Lappert, F.R.S.(University of Sussex), "Approaches to asymmetric syntheses and catalyses using electron-rich olefins and some of their metal complexes".

15 November — Dr. G. Bertrand (University of Toulouse, France), "Crutius rearrangement in organometallic series. A route for hybridised species".

24 November — Prof. G.G. Roberts (Applied Physics, University of Durham), "Langmiur-Blodgett films: Solid state polymerisation of diacetylenes".

2 December — Dr. G.M. Brook (University of Durham), "The fate of the ortho-fluorine in 3,3-sigmatropic reactions involving polyfluoroaryl and -heteroaryl systems".

8 December — Dr. G. Wooley (Trent Polytechnic), "Bonds in transition metal-cluster compounds).

1983

12 January — Dr. D.C. Sherrington (University of Strathclyde), "Polymer-supported phase transfer catalysts".

9 February — Dr. P. Moore (University of Warwick), "Mechanistic studies in solution by stopped flow F.T.-N.M.R. and high pressure NMR line broadening".

21 February — Dr. R. Lynder-Bell (University of Cambridge), "Molecular motion in the cubic phase of NaCN ".

2 March — Dr. D. Bloor (Queen Mary College, University of London), "The solid-state chemistry of diacetylene monomers and polymers".

8 March — Prof. D.C. Bradley, F.R.S. (Queen Mary College, University of London), "Recent developments in organo-imido-transition metal chemistry".

9 March — Dr. D.M.J. Lilley (University of Dundee), "DNA, Sequence, Symmetry, Structure and supercooling".

11 March — Prof. H.G. Viehe (University of Louvain, Belgium), "Oxidations on Sulphur", "Fluorine substitutions in radicals".
[The W.K.R. Musgrave Lecture].

16 March — Dr. I. Gosney (University of Edinburgh), "New extrusion reactions: Organic synthesis in a hot-tube".

25 March — Prof. F.G. Baglin (University of Nevada, U.S.A.,), "Interaction induced Raman spectroscopy in supra-critical ethane".

21 April — Prof. J. Passmore (University of New Brunswick, U.S.A. "Novel selenium-iodine cations".

4 May — Prof. P.H. Plesh (University of Keele), "Binary ionisation equilibria between two ions and two molecules. What Ostwald never thought of".

10 May — Prof. K. Burger (Technical University of Munich,FRG), "New reaction pathways from trifluoromethyl-substituted heterodienes to partially fluorinated heterocyclic compounds".

11 May — Dr. N. Isaacs (University of Reading), "The Application of high pressures to the theory and practice of organic chemistry".

13 May — Dr. R. de Koch (Caloin College, Grand Rapids, Michigan/Free University Amsterdam) "Electronic structural calculations in organometallic cobalt cluster molecules. Implications for metal surfaces"

16 May — Prof. R.J. Lagow (University of Texas, U.S.A.), "The chemistry of polylithium organic compounds. An unusual class of matter".

18 May — Dr. D.M. Adams (University of Leicester), "Spectroscopy at very high pressures".

25 May — Dr. J.M. Vernon (University of York), "New heterocyclic chemistry involving lead tetraacetate".

15 June — Dr. A. Pietrzykowski (Technical University of Warsaw/University of Strathclyde), "Synthesis, structure and properties of Aluminoxanes".

22 June — Dr. D.W.H. Rankin (University of Edinburgh), "Floppy molecules - the influence of phase on structure".

5 July — Prof. J. Miller (University of Camfinas, Brazil), "Reactivity in nucleophilic substitution reactions".

5 October — Prof. J.P. Maier (University of Basel, Switzerland), "Recent approaches to spectroscopic characterization of cations".

12 October — Dr. C.W. McLeland (University of Port Elizabeth, Australia), "Cyclization of aryl alcohols through the intermediacy of alkoxy radicals and aryl radical cations".

19 October — Dr. N.W. Alcock (University of Warwick), "Aryl tellurium (IV) compounds, patterns of primary and secondary bonding".

26 October — Dr. R.H. Friend (Cavendish Laboratory, University of Cambridge), "Electronic properties of conjugated polymers".

30 November — Prof. I. Cowie (University of Stirling), "Molecular interpretation of non-relaxation processes in polymer glasses".

14 December — Prof. R.J. Donovan (University of Edinburgh), "Chemical and physical processes involving the ion-pair states of the halogen molecules".

1984

10 January — Prof. R. Hester (University of York), "Nanosecond laser spectroscopy of reaction intermediates".

18 January — Prof. R.K. Harris (University of East Anglia), "Multi-nuclear solid state magnetic resonance".

8 February — Dr. B.T. Heaton (University of Kent), "Multi-nuclear n.m.r. studies".

15 February — Dr. R.M. Paton (University of Edinburgh), "Heterocyclic syntheses using nitrile sulphides".

7 March — Dr. R.T. Walker (University of Birmingham), "Synthesis and biological properties of some 5-substituted uracil derivatives; yet another example of selendipity in antiviral chemotherapy".

21 March — Dr. P. Sherwood (University of Newcastle), "X-ray photoelectron spectroscopic studies of electrode and other surfaces".

2. DURHAM UNIVERSITY CHEMICAL SOCIETY LECTURES

1982

28 January — Prof. I. Fells (University of Newcastle upon Tyne), "Balancing the Energy Equations".

11 February — Dr. D.W. Turner (University of Oxford), "Photoelectrons in a Strong Magnetic Field".

18 February — Prof. R.K. Harris (University of East Anglia), "N.m.r. in the 1980s".

25 February — Prof. R.O.C. Norman, F.R.S. (University of York), "Turning Points and Challenges for the Organic Chemist".

4 March — Dr. R. Whyman (I.C.I. Ltd., Runcorn), "Making Metal Clusters Work".

14 October — Mr. F. Shenton (County Analyst, Durham), "There is death in the pot".

28 October — Prof. M.F. Lappert, F.R.S. (University of Sussex), "The Chemistry of Some Unusual Subvalent Compounds of the Main Group IV and V Elements".

4 November — Dr. D.H. Williams (University of Cambridge), "Studies on the Structures and Modes of Action of Antibiotics".

11 November — Dr. J. Cramp (I.C.I. Ltd.), "Lasers in Industry".

25 November — Dr. D.H. Richards, P.E.R.M.E. (Ministry of Defence), "Terminally Functional Polymers , their Synthesis and Uses".

1983

27 January — Prof. D.W.A. Sharp (University of Glasgow), "Some Redox Reactions in Fluorine Chemistry".

3 February — Dr. R. Manning (Department of Zoology, University of Durham), "Molecular Mechanisms of Hormone Action".

10 February — Sir Geoffrey Allen, F.R.S. (Unilever Ltd.), "U.K. Research Ltd.".

17 February — [R.S.C. Centenary Lecture] Prof. A.G. MacDiarmid, (University of Pennsylvania), Metallic Covalent Polymers: $(SN)_x$ and $(CH)_x$ and their Derivatives".

3 March — Prof. A.C.T. North (University of Leeds), "The Use of a Computer Display System in Studying Molecular Structures and Interactions".

20 October — Prof. R.B. Cundall (University of Salford), "Explosives".

3 November — Dr. G. Richards (University of Oxford), "Quantum pharmacology".

10 November — Dr. J. Harrison (Sterling Organic), "Applied Chemistry and the Pharmaceutical industry".

24 November — Prof. D.A. King (University of Liverpool), "Chemistry in two dimensions".

1 December — Dr. J.D. Coyle (The Open University), "The problem with sunshine".

1984

26 January — Prof. T.L. Blundell (Birkbeck College, London), "Biological recognition: Interactions of macro-molecular surfaces".

2 February — Prof. N.B.H. Jonathan (University of Southampton), "Photoelectron spectroscopy - a radical approach".

16 February — Prof. D. Phillips (The Royal Institution), "Luminescence and photochemistry - a light entertainment"

23 February — Prof. F.G.A. Stone, F.R.S. (University of Bristol), "The use of carbene and carbyne groups to synthesise metal clusters".
[The Waddington Memorial Lecture].

1 March — Prof. A.J. Leadbetter (Rutherford Appleton Labs.), "Liquid Crystals".

8 March — Prof. D. Chapman (Royal Free Hospital School of Medicine, University of London), "Phospholipids and biomembranes: basic structure and future techniques"

28 March — [R.S.C. Centenary Lecture]
Prof. H. Schmidbaur (Technical University of Munich, FRG), "Ylides in coordination sphere of metals: synthetic, structural and theoretical aspects".

(B) RESEARCH CONFERENCES ATTENDED

Annual Chemical Congress of the Royal Society of Chemistry, Aston in Birmingham, 30 March-2 April 1982.

Graduate Symposium, Durham, 21 April 1982.

Annual Chemical Congress of the Royal Society of Chemistry, Lancaster, 11-13 April 1983.

186th American Chemical Society National Meeting, Washington, D.C., U.S.A., 28 August-2 September 1983.

A paper was presented by the author titled "Perfluoro-1,2,3-triazine derivatives as a route to azetes", R.D. Chambers and M. Tamura.

17th Sheffield Symposium on "Modern Aspects of Stereochemistry", Sheffield, 21 December 1983.

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